A Study for Enhancing Yield of Caustic Soda in Causticization Reaction for Industrial Application

By

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CERTIFICATION OF THESIS WORK

We the undersigned, glad to certify that **Md. Shahinoor Islam,** candidate for the degree of Master of Science in Engineering (Chemical) has presented his thesis work on the subject, "**A Study for Enhancing Yield of Caustic Soda in Causticization Reaction for Industrial Application**," The thesis is acceptable in form and content. The student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on October 07, 2007.

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ABSTRACT

This is an experimental investigation to find out yield of caustic soda in causticization reaction for industrial application. Commercial and analytical grades of sodium carbonate and lime were used to carry out the reaction. Industrially single stage causticization is used to produce caustic soda and theoretical yield cannot be achieved by single stage causticization. To increase conversion, the reactions were carried out in two and three stages. Two stage causticization was found to be good enough to achieve the maximum conversion for the concentration of sodium carbonate used in this work.

The reaction was carried out under established conditions; at 90^0C and at atmospheric pressure. The optimum time to carry out the reaction was 2.5 hours. In the selected two stage causticization process, first stage was carried out keeping lime as limiting reactant while the second stage was performed with excess lime. The first stage inlet composition of the reactants was 10.22% Na_2CO_3, 1.15% NaOH, 6.42% $Ca(OH)_2$ while that for the second stage was 1.62% Na_2CO_3, 8.6% NaOH, 1.7% $Ca(OH)_2$. The filtrates from the washing of calcium carbonate were used to prepare all solutions for reactions.

The conversion of sodium carbonate from first stage was 85.64-86.72% and 87.6-88.1 for analytical grade and commercial grade reactants respectively. The overall conversions of sodium carbonate for both grades were 93 to 94% in two stage causticization. Calcium oxide conversion from first stage was about 94.8-95.2% and 97-97.5% for analytical grade and commercial grade reactants respectively.

The byproduct calcium carbonate obtained from the process was very pure and it was comparable with the commercially available precipitated calcium carbonate produced from carbonation method. The byproduct calcium carbonate contained 98.3% and 96.67% calcium carbonate by weight for analytical and commercial grades respectively. It's crystal structure was calcite.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Caustic soda, soda ash, sulfuric acid and chlorine are the most extensively used chemicals in industries. The former two are known as alkalis. Industrially caustic soda is produced by chemical process and electrolytic process. The caustic soda produced is supplied to the industrial consumers either as concentrated solution or as solid packed in iron drums. Pure caustic soda is supplied to laboratories in the form of sticks or beads.

The chemical process is the classical method of caustic production. In this process, a solution of sodium carbonate is treated with excess calcium hydroxide producing liquid caustic and precipitated calcium carbonate. The precipitated calcium carbonate formed in this process is handled in three following different ways[1]:

- "reburned" in long rotary kilns to recover lime for use in process
- sent to cement plant for use as one of its main raw materials of cement manufacture
- sent to waste when it cannot be sold

Electrolytic methods for caustic production can be divided as

1. mercury cell
2. diaphragm cell, and
3. membrane cell process

Each process works by the electrolytic decomposition of purified brine to produce weak caustic solutions, chlorine and hydrogen. With the introduction of electrolytic methods for caustic and chlorine production, the lime soda process declined. Initially mercury cell process (Europe and Far East) and diaphragm cell process (North America) were used for caustic production. But in view of the hazardous nature of mercury and high salt content of diaphragm cell caustic, membrane cell process for caustic production has become preferred process[7]. Membrane cell is an improvement over diaphragm cell in which a semi permeable membrane separates the brine at the anode from the cathode. The membrane only allows the transfer of cations and prevents the contamination of caustic at the cathode by chloride ions[7]. In 2005 the global production capacity was 60 million tons of caustic soda and 55 million tons of chlorine[17].

In Bangladesh a mercury caustic-chlorine plant of capacity 2,000 t per year was set up in 1953 at Karnaphully Pulp and Paper mills. The plant is still running at its installed capacity. Another mercury cell caustic plant was installed in 1966 at Chittagong Chemical Complex, an enterprise of Bangladesh Chemical Industries Corporation, and it could produce 4,500 t caustic soda per year. The plant was refurbished with membrane cell technology by replacing mercury cells and it used to produce 7,000 t caustic soda per year till its closure in June, 2002. Global Heavy Chemicals limited, a private sector enterprise started production of 10,000 t caustic soda per year by using membrane cell process in 2002. Recently they have increased their production capacity to 18,000 t per year[17].

The present yearly demands for caustic soda and chlorine in Bangladesh are 80,000 t and 3600 t respectively. The demand for chlorine is being met while the production capacity of caustic soda is only 20,000 t per year. The rest 60,000 t of caustic soda per year is imported[17]. Because of limited demand of chlorine, the growth of chlor-alkali industry in Bangladesh has been stalled. Considering reality in Bangladesh, lime-soda process can be the right route for making caustic soda for certain applications. Moreover, it requires less investment per unit capacity against the membrane cell process.

"The production of caustic soda by [i.e. the Solvay + soda-lime processes] is technically possible but generally reckoned to be uneconomic. Production of soda ash via the Solvay process costs around $150 per ton. About 1.35 tons of soda ash needs to make 1 ton of caustic soda, so the raw material cost is about $200 per ton, plus the cost of the lime. Then the conversion of soda ash to caustic soda, the lime-soda process, requires a cost of around $150 per ton, so the caustic soda has a final cost of $350 per ton. This looks okay today when caustic soda sells for around $350-375 per ton in the U.S.A. and Europe, but prices in Asia are only $250 per ton or less. Of course under certain circumstances the costs mentioned can be lower, especially in locations where energy is cheap. But it should be remembered that today prices for caustic soda are especially high, and during a recession they can fall to $150 per ton or even less. At such times it is the return from sales of chlorine or chlorine derivatives that support the economics of the usual electrolytic route to chlor-alkali. Because of this the Solvay + lime-soda route to caustic soda has been virtually abandoned in the world[13]*."*

Thus the profitability of lime-soda process largely depends on the quality of the byproduct precipitated calcium carbonate and its efficient recovery. In most cases the sludge from lime- soda process is burnt to recover lime. Hence, the sludge from the lime-soda process did not receive much attention. White color, low alkalinity, freedom from harmful impurities and non abrasiveness are some prime requisites of calcium carbonate for use as a whitening, filler and coating. If product precipitated calcium carbonate can be produced in such form by doing any modification of the process, the process may be attractive one like chlor-alkali process. Multi-stage causticization can pave the way for achieving equilibrium conversion of sodium carbonate to sodium hydroxide as well as obtaining purer calcium carbonate in the first stage by using lime as the limiting reactant.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background

Caustic soda became known as a chemical only after production of soda ash. With the development of the Leblanc process for making soda ash from sea salt, caustic soda has been produced industrially by adding calcium hydroxide to soda ash as a batch process. The first Leblanc process plant was established in 1791. The scale-up of the process suffered setback due to French revolution and high British tariffs on salt until 1824. In 1861, the Belgian chemist Ernest Solvay developed a more direct process for producing soda ash from sodium chloride and limestone through the use of ammonia. Following the development of Solvay process of making soda ash, the caustic soda production process became more popular and economic[1].

Although electrolytic production of caustic soda was known in the 18th century, the process did not achieve commercial significance until the equipment became available for generating the huge amount of direct current required in the latter part of the 19th century. The developments of both the diaphragm cell and mercury cell processes for brine electrolysis took place during the period from 1883 to 1893[3].

The most vital component of a practicable diaphragm cell is a porous chemically resistant diaphragm which was invented in 1886. It was used by Greisheim Company in Germany in a 300 kW cell with potassium chloride as electrolyte. The first diaphragm cell in the United States was built in 1893 in Rumford Falls, N.Y. [3].

The first mercury cell of industrial significance was invented by Hamilton Young Castner in 1892. The process was developed to make a very pure caustic soda, which Castner believed was necessary for the electrochemical production of metallic sodium. This process employed the electrolysis of sodium chloride solution using a moving liquid mercury cathode to produce chlorine at the anode and a sodium-mercury amalgam at the cathode[3]. This so-called "mercury cell process" constituted the main commercial production process for chlorine and caustic soda from the 1890s to the middle of the 20th century.

Although mercury cells are still in operation throughout the world, they are being increasingly replaced with alternative mercury-free electrolytic processes. These processes, the diaphragm cell and membrane cell processes, produce chlorine and caustic soda, use the same basic raw materials (brine, water, and electricity), and are similar in terms of generating and treating product gases. They are similar to the mercury cells. The primary difference is the absence of mercury in effluents and emissions coming from diaphragm and membrane cells[3].

For the electrolytic production of caustic soda, diaphragm cells predominate in the United States, whereas mercury cells are predominant in Europe and Far East. There are a number of factors that have contributed to these preferences[3]:

- the relatively high voltage drop of mercury arc rectifiers used to supply d-c power discouraged the use of large single cells (low voltage, high current) in Europe, and favored the use of a number of smaller cells operated in series (high voltage, low current).
- asbestos, needed for diaphragms, is native to Canada and the northern United States; mercury is produced in Spain and Italy.
- energy needed for evaporation of water to concentrate dilute caustic effluent from diaphragm cells has been more plentiful and lower in cost in the United States than Europe.
- salt used for chlorine production in Europe, Japan, and Italy traditionally have been supplied and transported in the solid form, which is ideal for use in mercury cells.
- European consumers developed an early preference for the higher purity in mercury cell process.

Thus European producers found little interest to make diaphragm caustic with its higher salt content. Salt contamination problem of the diaphragm cell has led to the development of the membrane cell which produces higher purity caustic [3].

During the 1980s and 1990s, significant improvements in chlor-alkali technology have occurred with membrane cell technology. Recent improvements in commercial membrane electrolyzers have been directed at reducing cell voltage, increasing current density, and increasing membrane life[14].

Globally, the diaphragm cell process is expected to continue a slow decline, while the mercury cells process a more rapid decline. These declines will be offset by an increase in the membrane cell process. In 2002 the mercury cell process had about one fourth of world capacity; and the membrane and diaphragm cell processes shared the remaining capacity about equally. Membrane cell use has increased at a linear rate since 1980[14].

Even though mercury cell use is slowly declining in Western Europe, it still makes up over 50 percent of their capacity with the balance of capacity split evenly between membrane and diaphragm cells. Mercury cell use in Japan was banned by the Japanese government in 1986. Japan's chlor-alkali capacity is based exclusively on membrane cell technology. About 67 percent of U.S. capacity lies with diaphragm cell plants, and the corresponding percentage is about 53 percent in Canada[14].

The geographic distribution of chlor-alkali processes world-wide differs appreciably (production capacity of chlorine)[15]:

- Western Europe, predominance of mercury cell process (June 2000): 55%
- United States, predominance of diaphragm cell process: 75%
- Japan, predominance of membrane cell process: >90%

The remaining chlorine production capacity in Western Europe consists of (June 2000) diaphragm cell process 22%, membrane cell process 20% and other processes 3%[15].

Even though electrolytic caustic soda was produced in the 1890s, the lime soda process remained dominant until the late 1940s. During the early part of the 20th century, chemical caustic, manufactured primarily by ammonia soda producers, far outshadowed electrolytic caustic, but in the late 1930s production of electrolytic caustic surpassed the production of chemical caustic and has remained in the lead ever since. The percentage of total production by the electrolytic process was 29% in 1925, 44% in 1935, and more than 85 % in 1954. Figure 2.1 and 2.2 show the relative production of chemical and electrolytic caustic in the early part of the 20th century[1,6].

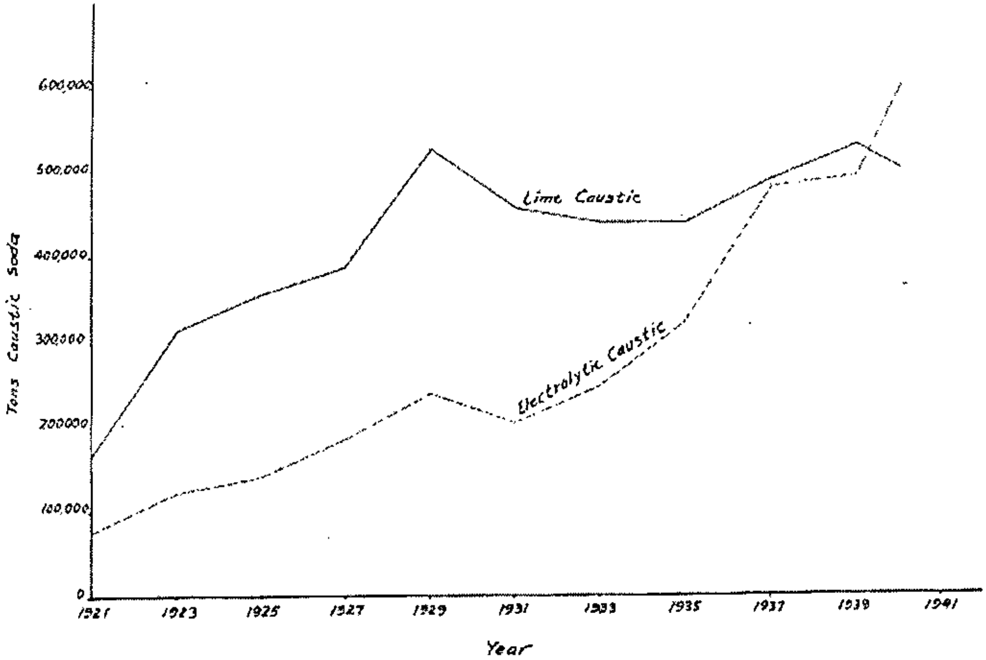


Figure 2.1: Comparative study between lime caustic and electrolytic caustic soda during early 20th century [1]

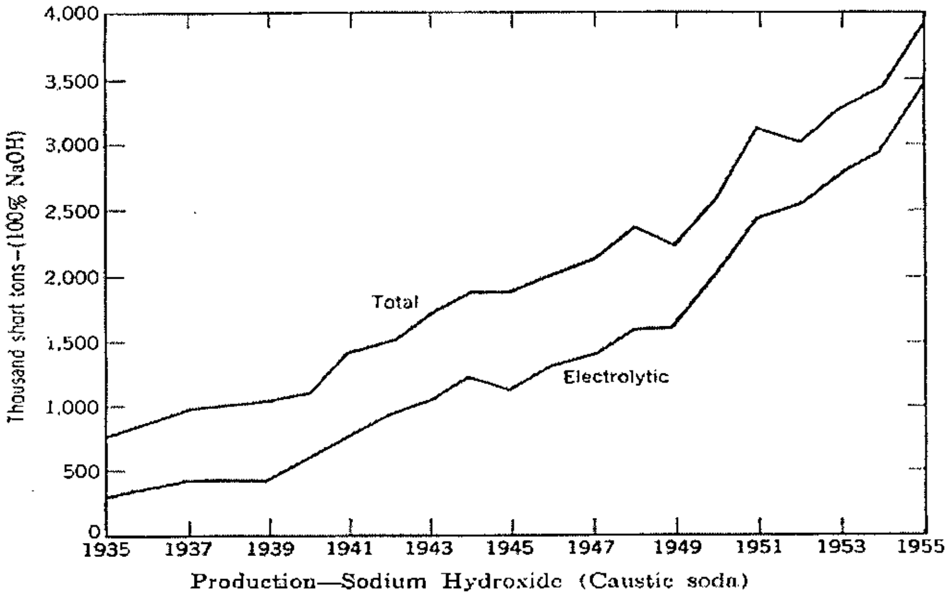


Figure 2.2: Comparative study between total and electrolytic production of caustic soda[6]

Incompleteness of the reaction made early caustic production heavily contaminated with soda ash. As reaction conditions became better known, relatively pure caustic soda was produced in large quantities until World War I. Since 1968, caustic soda has been produced exclusively by electrolysis in the United States, and however, caustic soda continues to be produced from soda ash only in isolated areas throughout the world[3].

The lime-soda process is still employed in small-scale production for captive plant consumption. Of particular importance is the Kraft recovery process, in which "green" liquor (an aqueous solution of sodium carbonate) is limed to produce "white" liquor or caustic soda, for return to the pulp digesters. The process also finds limited use in the production of alumina, in which lime and soda are charged to bauxite digesters. Under the digester operating conditions, the reaction is not complete, resulting in a loss of efficiency and other difficulties. Consequently, most alumina plants prefer to charge caustic soda directly to the digesters[3].

The electrolytic plants for caustic production need large initial capital investment and are economically attractive for large scale production. Moreover, there must also exist a ready market for the chlorine produced which in fact, is the main product with caustic soda as byproduct. In developing countries with capital constraints, the lime soda process is still attractive for small scale caustic production[9].

2.2 Properties of Caustic Soda

2.2.1 Physical Properties

Caustic soda is a clear white, highly hygroscopic solid and its solution is highly alkaline. It is very highly corrosive to skin. Table 2.1 lists some physical properties of solid caustic soda.

Table 2.1: Physical properties of caustic soda

Molecular weight	39.998
Density and phase	2.1 g/cm^3, solid
Index of refraction	1.3576
Latent heat of fusion	167.4 J/g
Solubility in water	111 g/100 ml (20°C)
Melting point	318°C (591 K)
Boiling point	1390°C (1663 K)
Basicity (pK_b)	0.2

In water solution depending on concentration, caustic soda can form five hydrate containing 1, 2, 3, 5, and 7 molecules of water, respectively. Hydrate formation is exothermic; caustic solution generates heat when further diluted with water. Any dilution of caustic from concentrations greater than 25% should be done cautiously[3].

2.2.2 Chemical Properties

Reaction with Metals: Caustic soda is highly reactive with amphoteric metals and their oxides form soluble salts. For example, hydrated alumina forms sodium aluminate.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

It also helps to form precipitate of soluble metals from aqueous solution. For example:

$$MgSO_4 + 2NaOH \longrightarrow Mg(OH)_2\downarrow + Na_2SO_4$$

Reaction with Weak Acid Gases: Sodium hydroxide reacts with weak acid gases such as H_2S, CO_2 and SO_2 as shown below:

$$H_2S + 2NaOH \longrightarrow Na_2S + H_2O$$

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

Reaction with Acids: Sodium hydroxide reacts violently with acids and compounds such as acrylonitrile, acroleine, maleic anhydride.

Strong acid: $HCl + NaOH \longrightarrow NaCl + H_2O$

Weak acid: $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

It may form mixed explosives such as dichloroacetylene by reaction with chloroacetylenes.

2.3 Principal Uses and Consumption of Caustic Soda

Caustic soda is one of the very few chemicals finding a very broad range of applications. The major uses of caustic soda are[11]:

- direct application, mainly as a neutralizing agent, 54 percent (pulp and paper 24 percent; soaps and detergents 10 percent; alumina 6 percent; petroleum 7 percent; textiles 5 percent; water treatment 5 percent; miscellaneous 43 percent);
- organic chemicals, 35 percent (propylene oxide 23 percent; polycarbonate 5 percent; ethyleneamines 3 percent; epoxy resins 3 percent; miscellaneous 66 percent);

- inorganic chemicals, 11 percent (sodium/calcium hypochlorite 24 percent; sulfur-containing compounds 14 percent; sodium cyanide 10 percent; miscellaneous 52 percent).

2.4 Available Grades of Caustic Soda

Different grades of anhydrous caustic such as United States Pharmacopoeia (USP), Chemically Pure (C.P.), reagent, and commercial are available in the form of flakes, granulated, ground, sticks, lumps, and drops (pellets). The common grades based on sodium oxide (Na_2O) content are 60% (77.4% caustic soda), 70% (90% caustic soda), 74% (95.48% caustic soda), and 76% (98.06% caustic soda). Aqueous solutions (containing about 50% and 73% sodium hydroxide) are available[6].

Special Grades of Caustic Soda

Liquid caustic soda is available as a 50% solution in four grades; diaphragm, rayon, membrane and purified diaphragm. Regular grade 50% diaphragm-cell caustic is suitable for most end uses, and accounts for about 85% of the caustic soda consumed in the United States. Other uses, such as in rayon manufacture, the synthesis of alkyl aryl sulfonates, and the regeneration of anion exchange resins, require high purity caustic. Mercury-cell caustic satisfies these requirements easily. In order to compete for high purity markets, however, the producers of diaphragm-cell caustic have spent a great deal of time and effort on purification processes. Crystallization of caustic soda by cooling to form the monohydrate or dihydrate has been investigated extensively and proven technically feasible, although it has never been used commercially in the United States[3].

The ammonia extraction process, however, developed and patented by Pittsburgh Plate Glass (PPG) Industries, has been used for many years. Essentially anhydrous ammonia is mixed with 50% caustic which forms a two phase system. The ammonia phase extracts salt and sodium chlorate together with some caustic soda and water. The second phase, consisting of about 62% caustic soda, is essentially free of salt and sodium chlorate, but contains some ammonia. It is separated and flash-distilled in a fractionating tower which recovers nearly all anhydrous ammonia[3].The still bottoms of salt, sodium chlorate, and caustic soda are generally used by producers for their alkalinity value, e.g. the neutralization of acid. The 62% caustic is either diluted to 50% or else further evaporated to 73% or anhydrous grades for sale[3].

73% Caustic Soda

In the freezing-point curve as shown in Figure 2.3, there is a relatively flat area from 65-74% caustic soda. Over this range of concentrations, caustic soda freezes at about 62^{0}C, permitting it to be concentrated and shipped, with some latitude in the concentration. Nominal 73% caustic remains in the liquid state at a temperature of 62^{0}C, and can be handled as a liquid as long as it is kept above this temperature. However, at concentration greater than 74% the temperature required to keep the product liquid rises very sharply.

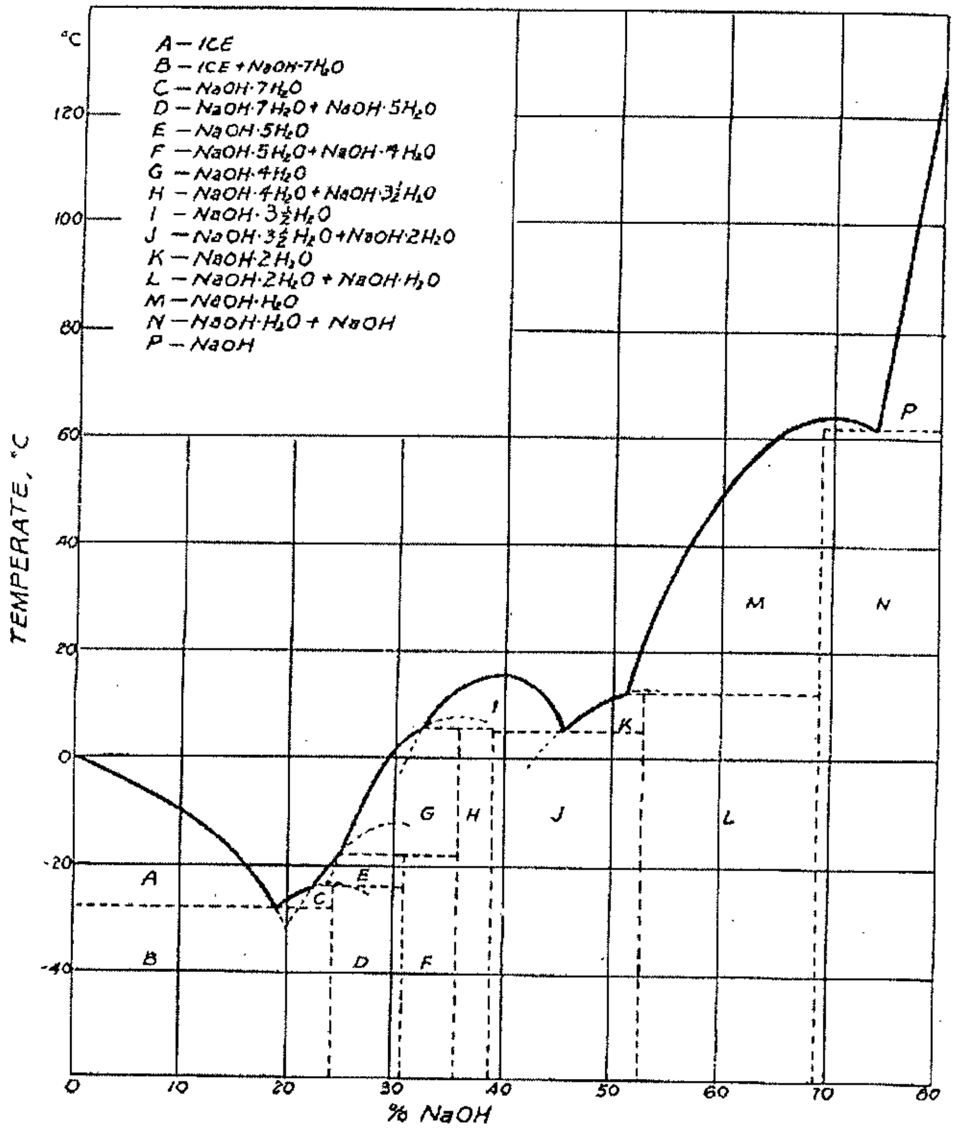


Figure 2.3: Freezing point diagram of pure caustic soda solution[1]

For storage, customers who buy the 73% caustic almost invariably dilute it to 50%, at which concentration it remains in the liquid state at room temperature. The objective of concentration, then, is to save freight costs by removing extra water. Using 50% caustic as feed, evaporation to 73% is usually accomplished in a single-effect, moderate-pressure, and natural-circulation evaporator. Nickel is required on the caustic side of the evaporator to avoid corrosion and iron contamination. Because no additional salt crystallization occurs, the complications of salt handling encountered, when concentration to 50%, are avoided. The evaporation system is usually controlled on the basis of specific gravity and temperature of the product. The product is stored and shipped at elevated temperatures in tanks with proprietary organic linings[3].

Either 73% regular or purified caustic can be produced using 50% regular or 62% ammonia extracted caustic, respectively, as the starting material. The determining factor in the use of 73% caustic is usually the cost of concentrating as opposed to the cost of shipping the extra water in a 50% solution[3].

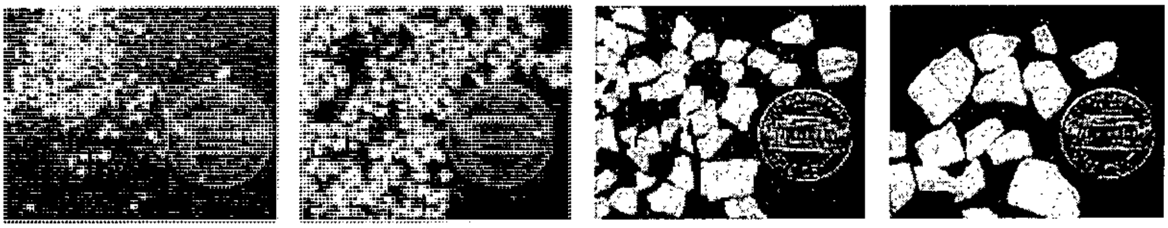
Anhydrous Caustic Soda

Prior to about 1950, anhydrous caustic was produced by evaporation of the water from 50% or 73% caustic solution in direct-fired cast-iron pots. In the production of high volume chemicals, however, the economics favor continuous process. For this purpose a tubular, flash-type evaporator was developed which is still being used. Heat is supplied by direct firing, by Dowtherm heat transfer fluid, or by a eutectic mixture of molten potassium nitrate, sodium nitrite, and sodium nitrate. Nickel or Inconel are commonly used as construction materials. Because sodium chlorate corrodes these metals at elevated temperatures, it must be removed or destroyed. This is not a serious problem with purified caustic, since chlorate has already been removed. However, a reducing agent such as sugar must be added to regular grade caustic before concentration[3].

Anhydrous caustic soda is marketed in four forms; beads, flakes, compounders and solid castings. These forms have the same chemical composition and differ only in particle size and shape. The packages for the anhydrous forms of caustic soda are shown in Table 2.2. Figure 2.4 shows different forms of solid caustic soda[11].

Table 2.2: Available solid forms of caustic soda in market

	Solid	Beads	Compounders	No. 4 Flake	No. 2 Flake
Available Packing	735-lb drums	500-lb drums 50-lb bags	450-lb drums	500-lb drums 100-lb drums 50-lb bags	500-lb drums 100-lb drums 50-lb bags
Dissolving Rates		15 Seconds	20 Seconds	41 Seconds	44 Seconds



(a) Beads (b) Compounders (c) Flake No. 4 (d) Flake No. 2

Figure 2.4: Available solid forms of caustic soda

2.5 Transportation

Caustic soda, liquid and dry, is regulated by the U.S. Department of Transportation (DOT) and is classified as a corrosive material. It must be transported in containers conforming to DOT specifications. DOT regulations covering handling and labeling must also be followed. The DOT identification number is UN I824 for liquid and UN I823 for anhydrous product. The Manufacturing Chemists Association (MCA), too, has a recommended warning label for container of both caustic soda solution and anhydrous caustic soda[3].

Approximately one fourth of the caustic soda produced in the United States is shipped in barges as 50% liquid. Tanks for shipping caustic soda usually insulated and equipped with external heating coils are made of nickel clad steel, or they are lined with an organic coating, to minimize iron contamination. Tank truck also plays an important role in the transportation of 50% caustic soda. Figure 2.5 shows the tank car for liquid caustic.

Caustic soda produced in anhydrous solid form is used by facilities that are not equipped to handle liquid caustic. Drums of 363 kg capacity are produced by pouring molten caustic into a drum and allowing it to solidify. Upon receipt, the steel drum is stripped away to yield a solid block of caustic soda[3].

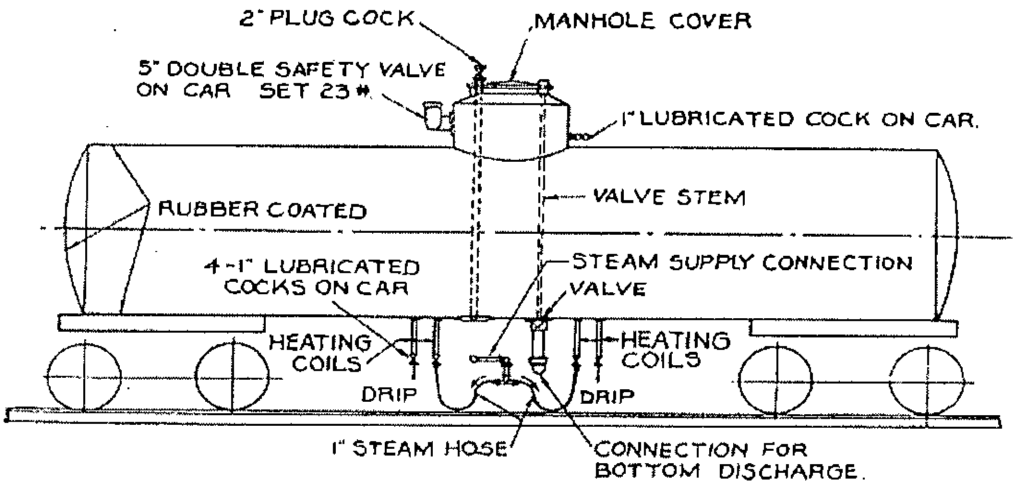


Figure 2.5: Tank car for liquid caustic[1]

2.6 Safety in Handling Caustic Soda

Caustic soda in any form must be respected by everyone who handles and uses it. Before starting to work with it, the user should be aware of its properties, know what safety precautions to follow, and know how to react in case of contact. Accidental exposure to caustic soda may occur under several conditions. Potentially hazardous situations include handling and packaging operations, equipment cleaning and repair, decontamination following spills and equipment failures. Employees who may be subject to such exposure must be provided with proper personal protective equipment and trained in its use[11].

2.7 Industrial Methods for Producing Caustic Soda

Sodium hydroxide, commonly called caustic soda, is produced commercially by two basic methods:

a) electrolytic cells and
b) chemical process

Most caustic soda is produced from electrolytic cells. There are three types of electrolytic cells: (i) mercury (ii) diaphragm and (iii) membrane.

In electrochemical process, an electric current is passed through a sodium chloride salt solution in specially designed cells, to produce sodium hydroxide. The salt solution is decomposed into 10 to 12 % sodium hydroxide solution, with hydrogen gas forming at the cathode and chlorine gas at the anode as co- products. Description of electrolytic process is given in **Appendix- F**.

Chemical process caustic soda is produced by reacting sodium carbonate (Na_2CO_3) with hydrated lime [$Ca(OH)_2$] to form sodium hydroxide (NaOH) and precipitated calcium carbonate ($CaCO_3$).

2.7.1 Chemical (Lime Soda) Process

In lime soda process, a solution of sodium carbonate (soda ash) is treated with calcium hydroxide (slaked lime) to produce a precipitate of calcium carbonate and an aqueous solution of sodium hydroxide. After removal of the insoluble carbonate, the solution is concentrated to give various grades of caustic soda for sale. The process may be operated as a batch or a continuous basis[1].

2.7.1.1 Chemical Reactions

The following reactions are involved in lime soda process:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (1)$$

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3 \qquad (2)$$

The reaction (2) is known as causticization reaction and depends upon the low solubility product of Ca^{++} and CO_3^{--} ions causing the removal of solid $CaCO_3$ from solution. As both sodium hydroxide and sodium carbonate are very soluble, the reaction depends upon the relative solubility of calcium carbonate and calcium hydroxide in the solution. As the reaction proceeds, the concentration of sodium hydroxide in solution increases. This increases common ion effect, and greatly decreases the solubility of calcium hydroxide until it is no more soluble than calcium carbonate, and the following equilibrium is set up:

$$Na_2CO_3 + Ca(OH)_2 \leftrightarrow 2NaOH + CaCO_3$$

Thus conversion of Na_2CO_3 to NaOH cannot proceed to completion. Consequently, at the end of the reaction in the resulting solution (lye), neither calcium carbonates nor calcium hydroxide can remain in solution to any large extent. That is to say, in the causticization reaction the equilibrium is reduced to that between sodium carbonate and sodium hydroxide in the resulting lye:

$$Na_2CO_3 + Ca(OH)_2(solid) \leftrightarrow 2NaOH + CaCO_3(solid)$$

Therefore, $K = \frac{(2Na^+)^2(2OH^-)^2}{(2Na^+)^2(CO_3^{--})} = \frac{(2OH^-)^2}{CO_3^{--}}$

To get high conversion (i.e., to get OH^- concentration in the solution as high as possible and CO_3^{--} concentration as low as possible), the value of K must be as high as possible. In the resulting lye, since the concentration of calcium hydroxide and calcium carbonate are small, it may be assumed that complete ionization takes place. Hence the solubility product of $Ca(OH)_2$ (K_1) is $(Ca^{++}) \times (2OH^-)^2 = 4(OH^-)^3$, and that of $CaCO_3$ (K_2) is $(Ca^{++}) \times (CO_3^{--}) = (CO_3^{--})^2$.

Therefore, $K = \frac{(2OH^-)^2}{CO_3^{--}} = \frac{\sqrt[3]{4K_1^{\ 2}}}{\sqrt{K_2}} = 1.59\frac{{}^{2/3}\sqrt{K_1}}{\sqrt{K_2}}$.

Thus K is a function of the solubility of calcium carbonate and calcium hydroxide. From the equation, the more soluble the calcium hydroxide and the less soluble its carbonate, the more suitable it will be as a causticizing agent. This is a general principle governing the choice of a causticizing agent for the conversion of sodium carbonate to sodium hydroxide.

From the above expression: $K = \frac{(2OH^-)^2}{CO_3^{--}}$

where, K is a constant at a given temperature, by dividing both sides by (CO_3^{--}) and extracting the square root, the expression becomes

$$\frac{(2OH^-)}{(CO_3^{--})} = \frac{K'}{\sqrt{(CO_3^{--})}}$$

where, K' is the square root of K.

From the expression it is clear that the more dilute the soda solution (i.e., the smaller the concentration of CO_3^{--}) is, the higher will be conversion percentage (i.e., the ratio of OH^-/CO_3^{--} increases as $\sqrt{CO_3^{--}}$ decreases)[1].

2.7.1.2 Factors Affecting Causticization

Factors that affect causticization reaction are:

a) temperature
b) duration of causticization
c) concentration of sodium carbonate solution and
d) quality of lime

a) Effect of Temperature on Conversion

Causticization reaction is an endothermic reaction. The optimum temperature for causticization reaction was studied by Mannan, 1998[9]. The causticization reaction was carried out using analytical and commercial grade reactants. He performed experiments keeping both reactants in stoichiometric proportion. Figure 2.6 shows his experimental results[9]. However, with increase in temperature the settling rate of calcium carbonate and the speed of reaction are increased.

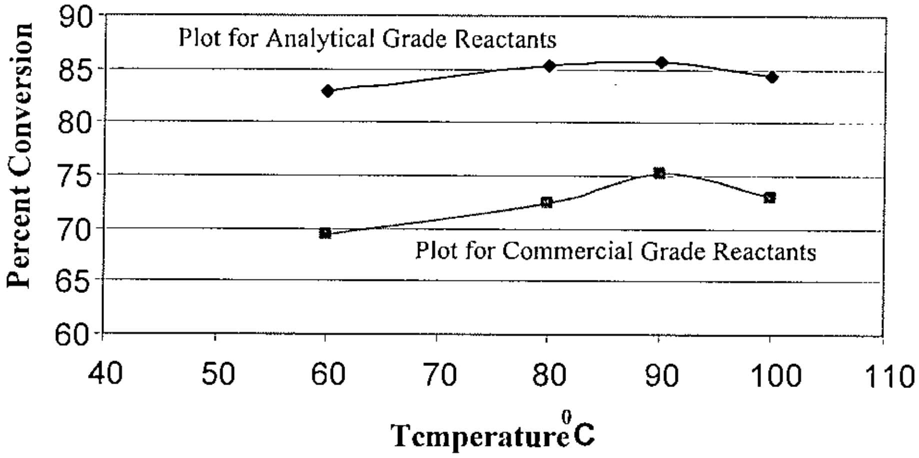


Figure 2.6: Effect of temperature on conversion of sodium carbonate (9)
(1 hr reaction time)

b) Duration of Causticization

Imtiaz, 1999[8], performed causticization reaction using both analytical and commercial grade reactants in the laboratory. He carried causticization in one stage at 90^0 C keeping 10% excess calcium hydroxide. He found out the percentage conversion of calcium hydroxide with time. Figure 2.7 shows his experimental findings. In the case of commercial grade reactants, the conversion after 120 min is about 78%. The same for analytical grade is about 80%. The optimum time for causticization is about 2.5 to 3 hours[8].

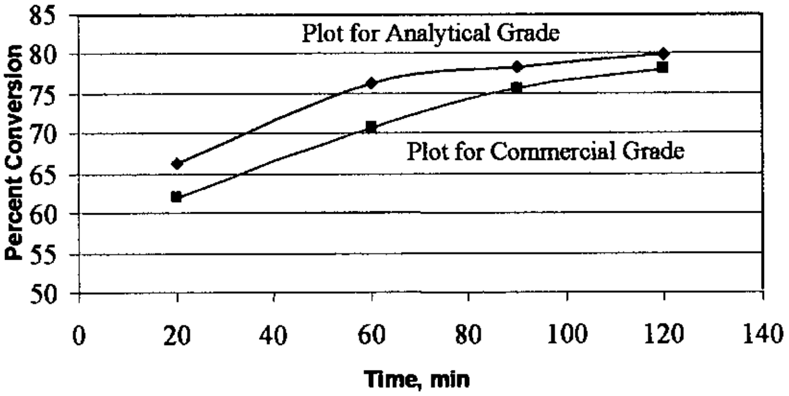


Figure 2.7: Effect of time on conversion of calcium oxide (8)

c) Initial Concentration of Sodium Carbonate

Figure 2.8 shows the theoretical conversion curve giving the percentage conversion from different concentrations of soda ash solution on the basis of using dry slaked lime. With 10% soda solution for instance, the theoretical conversion is 97%, but for the plant in operation, using 1.13 specific gravity liquor containing 12.5% sodium carbonate, the conversion ratio is not over 92 to 93%. In practice it does not average much over 90% conversion[1].

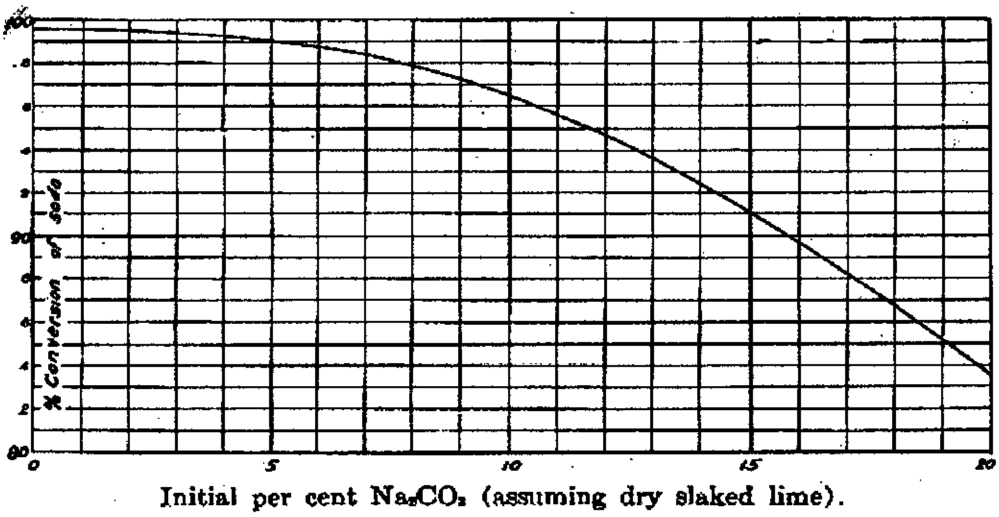


Figure 2.8: The causticization equilibrium curve

Dilute liquor requires an excessive amount of fuel for concentration of dilute caustic soda; hence a close study must be made between the degree of conversion obtainable and the cost of fuel for the concentration of the caustic lye. In actual practice, 11 to 12 percent sodium carbonate solution is used[4].

d) Effect of Quality of Lime

The standard composition for quicklime for use in causticizing shall contain 85 per cent of available lime. Lime containing more than 3 per cent magnesia or less than 70 per cent of available lime shall be rejected as uneconomical to use. It is recommended that a bonus or a penalty of 1.5 per cent of the contract price be added to or deducted from the payment for each 1 per cent of available lime above or below the standard 85 per cent. In choosing lime for causticizing, it is necessary to consider its physical as well as its chemical properties, because after the causticizing reaction has been completed, the caustic soda solution must be separated from the precipitated calcium carbonate and the ease with which this can be done is dependent to some extent on the physical properties of the lime used. The separation of the caustic soda solution from the calcium carbonate mud can be readily accomplished by decantation, preferably with countercurrent washing of the calcium carbonate, in a series of decantation tanks. Soon after Dorr thickeners were first applied to this problem of continuous countercurrent decantation, it became evident that the settling rates of the calcium carbonates produced at different plants varied widely, with a corresponding variation in the size of thickeners required handling a given tonnage of solids[22].

Factors Influencing Settling Rate

Among the factors which are considered to have an influence on the settling rate of the calcium carbonate sludge after causticizing are the following[22]:

1) **Source of lime**
    a) Chemical constitution
    b) Physical nature
2) **Method of burning the lime**
    a) Temperature
    b) Length of the burning period

3) **Method of slaking the lime**
    a) Degree of agitation during slaking
    b) Temperature during slaking
    c) Amount of water used
    d) Use of soda ash or caustic soda solutions for slaking
4) **Method of causticizing**
    a) Period of Agitation
    b) Temperature
    c) Violence of Agitation
    d) Excess of lime or soda ash used
5) **Causticity and concentration of caustic desired**
6) **Presence of impurities particularly when reburnt lime is used**

2.7.1.3 Batch Causticization Process

Figure 2.9 shows the block diagram of a batch process. Lime is used as milk of lime or in lumps. The soda ash solution is causticized in large tanks with flat bottoms in the desired proportion. This is mixed with wash water from a previous stage and agitated for two to three hours. The mixer then passes through decanters to remove the precipitated calcium carbonate from the caustic soda solution. The slurry still containing some caustic and is subjected to further washing and the washings being returned to the cycle again. The lime sludge practically free from caustic is either reburnt or discharged. The ten percent caustic solution from the decanter goes to the multiple effect evaporators, where it is evaporated to 50% caustic soda. Impurities such as soda ash, salt, sodium sulfate separate out and are allowed to settle down before final removal. If caustic flakes are desired, the solution is further concentrated to 75% in a single effect evaporator and then charged in direct fired thick grained cast iron pots. The product is sent to a flaker, where it is cooled to form flakes and packed in drums[4].

The sodium carbonate solution from the storage tank is run by gravity into the causticizer which may be 3 to 4.5 meters in diameter and 2.5 to 3 meters in height (depends on plant capacity). The tank is provided with steam line to heat the liquor to 80^0C to 90^0C. Compressed air is provided for agitation. The soda solution is adjusted to 10-11 percent dilution. A steel bucket of perforated bottom and sides with 6 mm hole is attached to the side of the causticizer and partially dipped in the soda solution. The tank is also provided with a mechanical agitator. Lime is added to steel basket as lumps smaller than 15 cm, the proportion to lime to soda ash as three to five. Sometimes the milk of lime is preferred to the lumps[4].

After the desired amount of lime has been added, the reaction is carried out for two to three hours; the liquor is allowed to settle for 1 to 3 hours. The clear solution containing about 10% caustic is withdrawn by applying decantation technique. The lime sludge is washed with the washing liquor of the previous batch, a number of such tanks being provided. The washing of sludge is usually done by counter current flow[4].

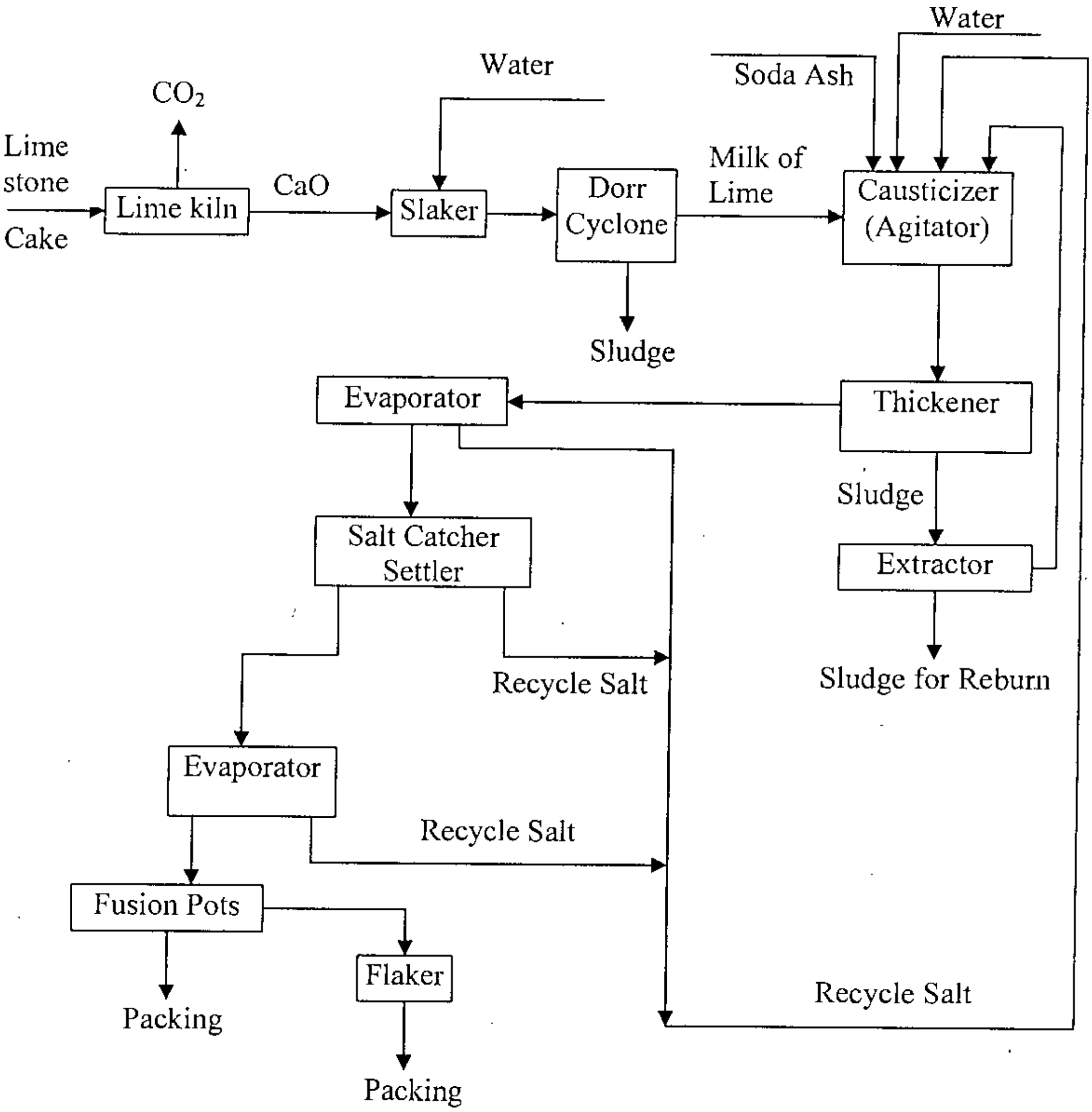


Figure 2.9: Block diagram of a caustic soda plant producing chemical caustic[4]

Washing

The lime sludge, with whatever lye remains, is washed with the third liquor from a previous batch, the stirrer is started, and the liquor heated with steam. After settling, this gives the second liquor of 5% sodium hydroxide. That may be added to the lye tank. This slime is again washed with the fourth liquor in a similar way; this gives the third liquor which is used for second washing for next batch and also for making soda solution for causticization. Finally the slime is further washed with fresh water, giving the fourth liquor. The washed slime, containing the precipitate of calcium carbonate with a little alkali that remains, is washed out and sent to waste.

A batch of causticization can be made in every 2.5 to 3 hours; but coupled with the time for washing, settling, and decanting, makes the cycle for each tank about 16 hours. This washing process is very important although it is tedious; considerable soda could be lost through careless washing[1].

2.7.1.4 Dorr Continuous Causticization Process

Dorr continuous causticizing process is a modern chemical process practice. It gives more thorough washing with a small quantity of water and stronger caustic lye to use in Dorr agitators and thickeners. Figure 2.10 shows a continuous Dorr causticizing plant. A large causticizing plant consists of Dorr agitators, thickeners, lime slaker, classifier, rotary filters, diaphragm pumps, and rotary lime kiln[1].

18-20 percent sodium carbonate solution is made in a rotary dissolver using the weak liquor from previous cycle. Lime is slaked to a dry hydrate in a rotary lime slaker using also the weak wash liquor. The hydrated lime coming from the slaker is then suspended in larger quantities of the weak wash liquor to form a strong milk of lime containing about 250 grams of CaO per litre. The milk of lime passes through a mechanical classifier in which unburnt stone, the finely divided overburnt lime, and sand are separated. The soda solution is first causticized with a large excess of lime in the primary causticizing agitators, generally three in series, from the last of which the lye suspension is then settled in large continuous thickeners. The overflow clear liquor from the first thickener (contains 11% sodium hydroxide and 1.7% sodium carbonate[6]) is withdrawn as product or sent to evaporators to be concentrated. The sludge from the bottom of the first

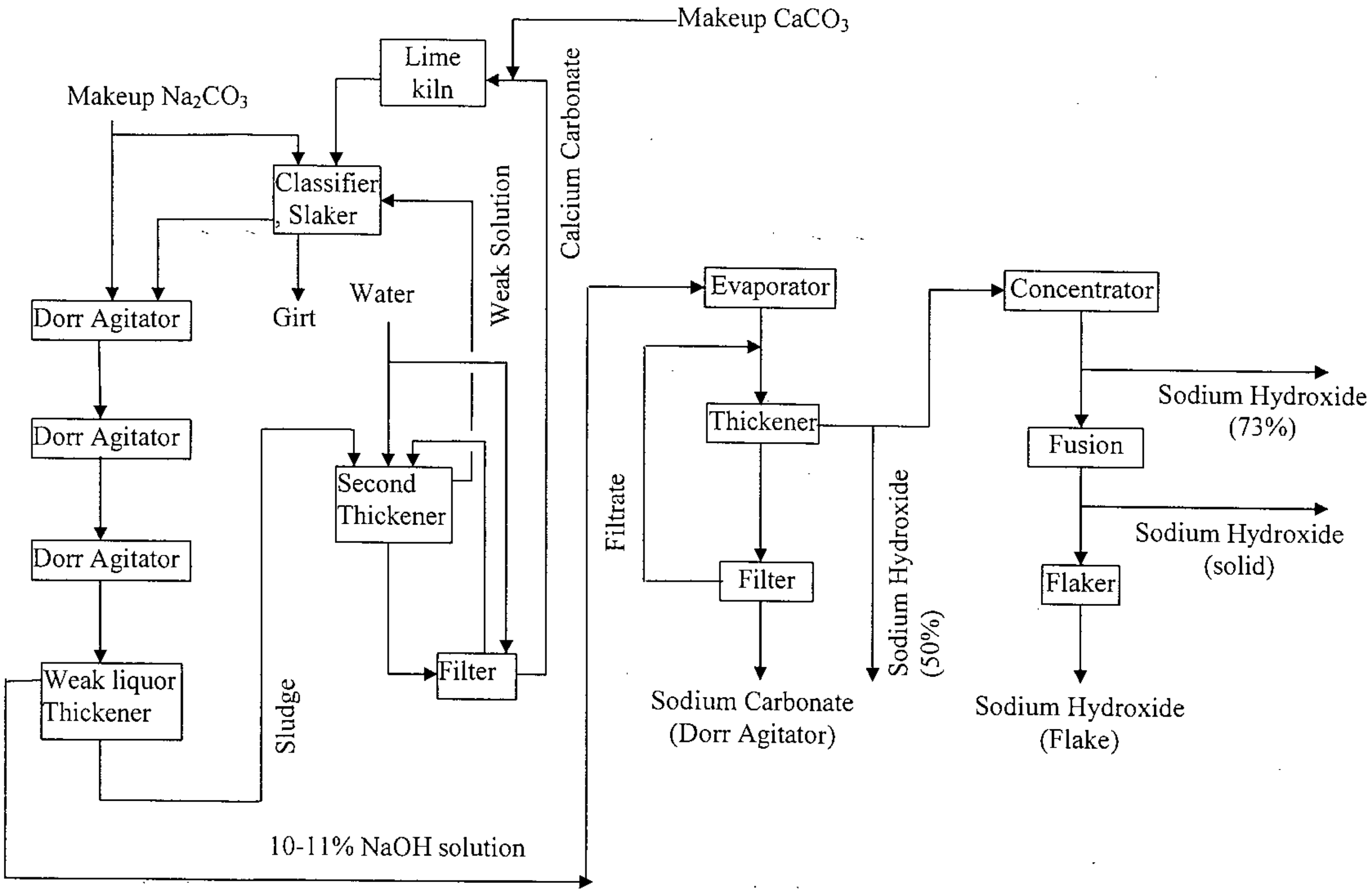


Figure 2.10: Dorr continuous causticization process[6]

thickener is pumped out by means of a diaphragm pump to a rotary drum filter (generally of Oliver type), from which the cake containing an excess of free lime is further treated with about 10% excess of weak soda solution in a secondary causticizing agitator. The filtered liquor from this filter is returned to the first thickener. From the secondary agitator the lye suspension is settled in the second thickener, the overflow from which furnishes the weak liquor for making soda solution in the dissolver and for hydrating the lime and making milk of lime in the lime slaker and classifier.

The sludge from the second thickener is pumped to the third thickener, in which fresh water is introduced for the final washing and from which the sludge is pumped to another rotary drum filter. Fresh water is also used on this filter to wash the cake and the filter water is returned to the third thickener. In this way, the recovery of alkali is as high as 99.7%. The upkeep is low, power consumption is quite reasonable, and the floor space required comparatively small[1].

2.7.1.5 Production of Caustic Soda from Pirssonite or Gaylussite

In this process caustic soda is prepared from naturally occurring alkaline minerals comprising double salts of sodium carbonate and calcium carbonate. The process comprises heating the said naturally occurring alkaline minerals to temperatures sufficient to dehydrate and partially decarbonate alkaline minerals and provide an intermediate product of a mixture of sodium carbonate and calcium oxide. This intermediate is then contacted with water to effect causticization of the sodium carbonate and provide a recoverable phase comprising an aqueous solution of caustic soda. Figure 2.11 shows the steps of production of caustic soda from gaylussite[18].

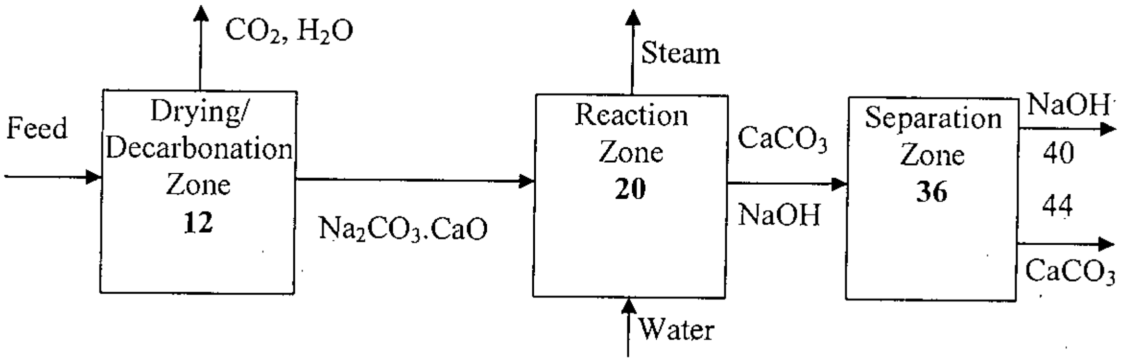


Figure 2.11: Steps of production of caustic soda from gaylussite[18]

Feed stream comprising of an alkaline mineral selected from the group consisting of pirssonite ($Na_2CO_3.CaCO_3.2H_2O$) and gaylussite ($Na_2CO_3.CaCO_3.5H_2O$) is introduced into drying/decarbonation zone in the form of a particulated solid; wherein the alkaline mineral is heated at a temperature of at least about 150^0 C to effect drying of the alkaline mineral and at a temperature about 750-850 ^{0} C to effect decarbonation of the particulated $CaCO_3$ solid mineral. The decarbonation temperature of Na_2CO_3 is greater than 850^0C. The effluent from the decarbonatior provides a hot, friable, solid intermediate product comprised of sodium carbonate and calcium oxide and is sent to causticizer[18].

The water required for effecting the causticization of the sodium carbonate in the dried and decarbonated intermediate product is introduced into reaction zone. The quantity of water introduced into causticizer will be an amount at least equivalent to the theoretical amount required to effect hydration of the calcium oxide in dried and decarbonated intermediate product. Generally, however, the quantity of water introduced into causticizer will be an amount in excess of the theoretical amount and sufficient to counteract the loss of water as steam. This steam, which is removed from reaction zone is generated by the contact of the water with the hot intermediate product as well as by the appreciable heat of hydration which occurs as the water and calcium oxide react to form the calcium hydroxide necessary for the causticization reaction. Therefore, in the practice of the process, the quantity of water introduced into reaction zone equal to the theoretical amount plus an excess of at least about five percent.Upon completion of the hydration and causticization in reaction zone the resulting product, which is a mixture of particulated solid calcium carbonate suspended in an aqueous solution of caustic soda is removed from reaction zone and conveyed therein to separation zone. Separation zone is capable of effective separation of the suspended calcium carbonate and aqueous caustic soda solution which then are removed from separation zone 36 through conduits 44 and 40, respectively as shown in Figure 2.11. Examples of vessels which can be employed to separate these materials include any of the known separation devices such as settling tanks, cyclones, filtration devices such as centrifuges and rotating drums, and the like.The aqueous caustic soda solutions prepared and recovered in accordance with the process of this invention will contain about 10 to 11 percent by weight of caustic soda. These solutions may be packaged and sold as it is or concentrated by known means to provide solutions containing up to 50 percent by weight or more of the caustic soda[18].

2.7.1.6 Process for Production of Caustic Soda and Calcium Carbonate Slurry

The process for obtaining a sodium hydroxide solution and slurry of fine calcium carbonate particles suitable for use as a paper coating or filler pigment includes the initial step of reacting a calcium hydroxide with sodium carbonate under conditions effective to produce aqueous slurry containing sodium hydroxide and calcium carbonate as a precipitate. The aqueous sodium hydroxide solution is then removed from the first slurry by suitable means such as filtration. The slurry is reconstituted, and a fine fraction comprising aqueous slurry of fine calcium carbonate particles is removed from by suitable means such as a classifying device. The second half of the process can be used independently to process mined calcium carbonate. This includes steps of classifying the carbonate slurry to remove a coarse fraction comprising carbonate particles larger than a predetermined particle size to obtain a slurry of fine carbonate particles, grinding the coarse fraction to reduce the size of carbonate particles therein to form a ground product, and reclassifying the coarse fraction to obtain an additional quantity of a slurry of fine carbonate particles. The ground product is preferably combined with fresh aqueous slurry to form a combined product, and the classifying step is repeated continuously or intermittently in a closed circuit using the combined product to obtain slurry of fine carbonates particles[19].

2.8 Byproduct Calcium Carbonate

2.8.1 Introduction

Calcium carbonate occurs in nature as limestone. Depending on the requirement, ground lime stone is sometimes directly used as whiting and filler. It is used for the production of lime. Quality and purity of these products depend mostly on the quality of the limestone. It may be classified according to origin, chemical composition, and texture of stone and geological formation. Chemically it consists primarily of calcium carbonate, and secondarily of magnesium carbonate with varying percentage of impurities. Limestone is generally classified into the following three types[8]:

Calcite: The carbonate content is essentially calcium carbonate with no more than 5% magnesium carbonate. Calcite that is fire white can be used in the manufacture of calcium carbonate pigment. Another variety that is off white, despite excellent chemical purity, is of little or no significance in the manufacture of pigments.

Magnesian: This contains both carbonates with a magnesium carbonate content of 5-20%.

Dolomite: Magnesium carbonate content of this rock is over 20% but no more than 45.6%, with the balance $CaCO_3$. It has no significance in the manufacture of pigments.

2.8.2 Impurities in Natural Calcium Carbonate

The chemical composition and properties of limestone depend on the nature of impurities and degree of contamination. It contains alumina, silica, iron, sodium, potassium, sulfur, and phosphorous compounds as impurities[8]. Table 2.3 shows composition of different types of limestone found in US.

Table 2.3 Composition of different types of limestone found in US[8]

Component	Calcite	Magnesian	Dolomite
CaO	54.54	45.65	31.2
MgO	0.59	7.07	20.45
CO_2	42.9	43.6	47.87
SiO_2	0.7	2.55	0.11
Al_2O_3	0.68	0.23	0.3
Fe_2O_3	0.08	0.2	0.19
SO_3	0.31	0.33	
P_2O_5		0.04	
Na_2O	0.16	0.01	
K_2O		0.03	
H_2O		0.23	
Other		0.06	

2.8.3 Properties of Calcium Carbonate

2.8.3.1 Physical Properties

Calcium carbonate occurs naturally in two crystal structures 'CALCITE' and 'ARAGONITE'. Calcite is thermodynamically stable at all investigated pressures and temperatures. Aragonite is metastable and irreversibly changes to calcite when heated in dry air to about 400^0C, the rate increasing with temperature. The transformation is much more rapid when contact with water or solutions containing calcium carbonate and may take place at room temperatures[3].The crystal form of calcite is hexagonal form and aragonite is in orthorhombic system. In the commercial forms of precipitated calcium carbonate, where aragonite predominates, crystals have parallel sides and large length to width ratios. Rapid precipitation, high concentration of reactants, high temperature and presence of divalent cations increases the tendency to produce aragonite[3]. Specifications of aragonite and calcite crystal structure are shown in Table 2.4 and Table 2.5.

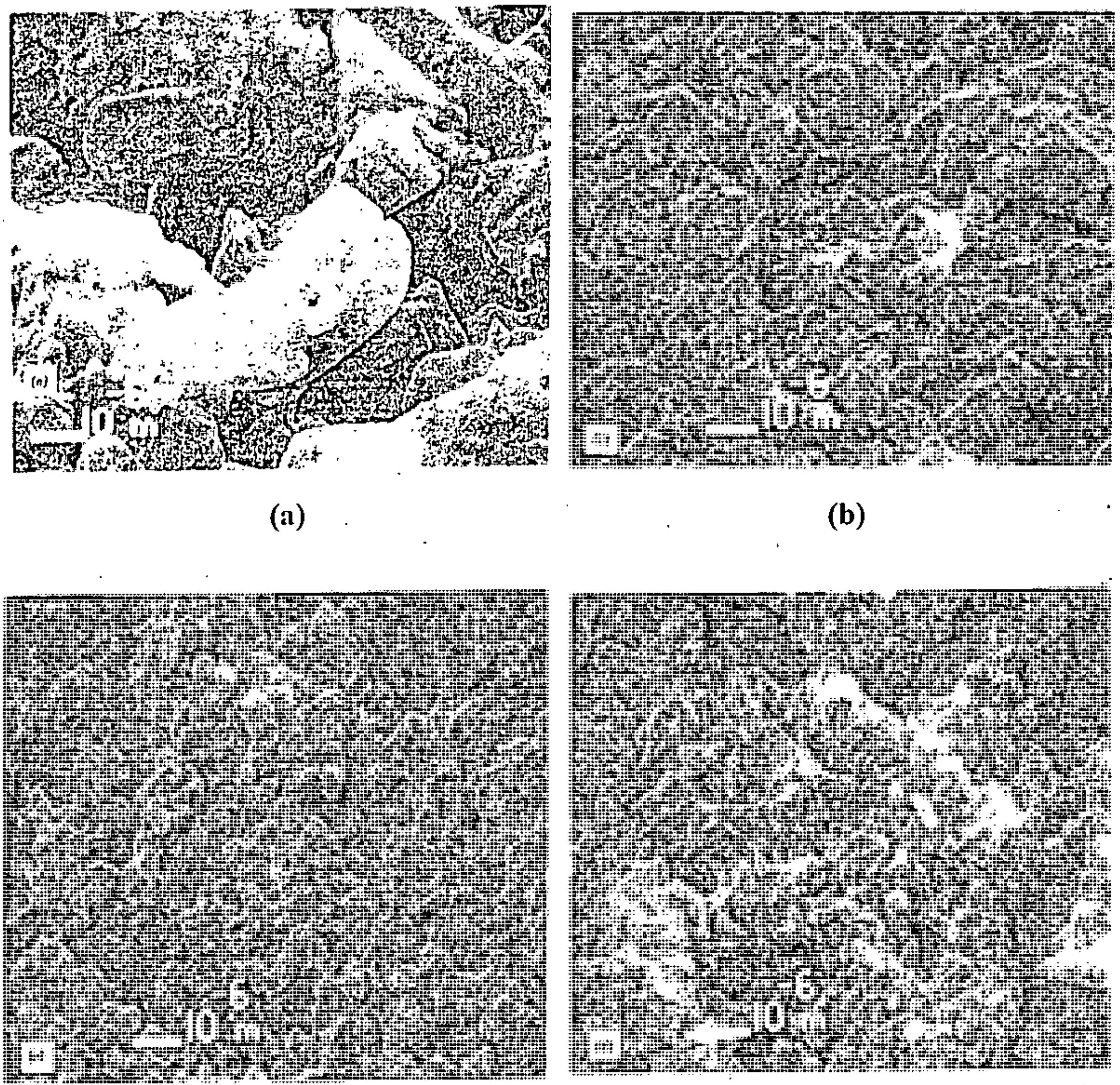
Table 2.4: Specifications of aragonite crystal structure[10]

Properties	Typical Values
Bulk density, g/ml	0.75-1.05 (Heavy) 0.6-0.75 (Medium) 0.36-0.58 (Light) 0.25-0.35(Extra light)
Loss on drying at 105± 5 deg C for 1 Hr max	0.6
pH (10% suspension)	9.8±0.3
Soluble alkali % Na_2O	0.25 max
Sieve residue on 325 mesh (43 micron) wet sieving	0.1 max
Particle size (Malvern) D 50 D 90 average	5-8 (microns) 10-18 (microns) 5-10 (microns)
Crystal structure	100% aragonite
Brightness	98% min
Oil absorption g/100g	25-50
Magnesia % $MgCO_3$ max	1.5
Acid insoluble, % max	0.2
Total assay % $CaCO_3$ min	97.5

Table 2.5: Specification of calcite crystal structure[10]

Properties	Typical Values
Bulk density, g/ml	0.75-1.05 (Heavy) 0.6-0.75 (Medium) 0.36-0.58 (Light) 0.25-0.35(Extra light)
Loss on drying at 105 ± 5 deg C for 1 Hr max	0.6
pH (10% suspension)	10.0±0.2
Soluble alkali % Na_2O	0.25 max
Sieve residue on 325 mesh (43 micron) wet sieving	0.1 max
Particle size (Malvern) D 50 D 90 average	2.5-5 (microns) 7.0-10 (microns) 3.0-6.0 (microns)
Crystal structure	100% calcite
Brightness	98% min
Oil absorption, g/100g	41-60
Magnesia % $MgCO_3$ max	1.75
Acid insoluble, % max	0.2
Total assay % $CaCO_3$ min	97.5

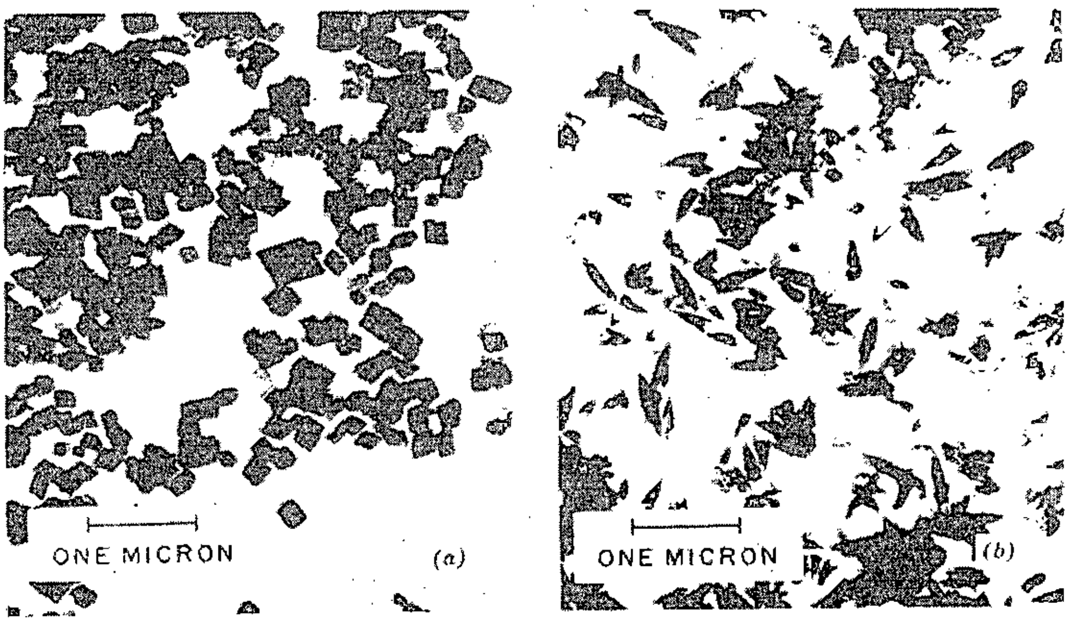
Figure 2.12 shows scanning photomicrographs of calcium carbonates[2]. Commercial precipitated calcium carbonate in the calcite form normally has either the rhombohedral or scalenhedral crystal habit as shown in Figure 2.13. One manufactured product claims to be of a novel crystal habit and is covered by patent as shown in Figure 2.14 (a). Commercial precipitated calcium carbonate in aragonite form is characterized by crystal having parallel sides and large length to width ratio as shown in Figure 2.14 (b).



(a) (b)

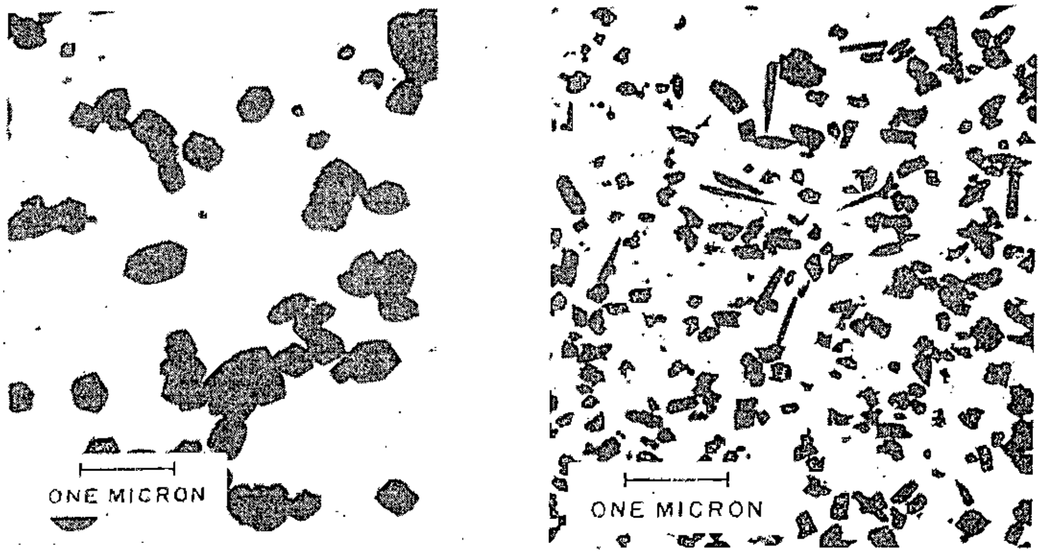
(c) (d)

Figure 2.12: Scanning photomicrographs of calcium carbonates showing (a) fine-grounded limestone (FGL); (b) ultrafine ground limestone (UFGL); (c) precipitated calcium carbonate, calcite (PCC-C); and (d) precipitated calcium carbonate, aragonite (PCC-A) (reference bar =1 micron)[2]



(a) (b)

Figure 2.13: Transmission photomicrographs showing precipitated calcite in (a) the rhombohedral form and (b) the scalenhedral form[2]



(a) (b)

Figure 2.14: Transmission photomicrographs showing precipitated (a) calcite in novel barrel-shaped prismatic form and (b) aragonite in acicular form[2]

2.8.3.2 Chemical Properties

Calcium carbonate shares the typical properties of other carbonates[16].

- It reacts with strong acids, releasing carbon dioxide:

  $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

- It releases carbon dioxide on heating to above 840°C in the case of $CaCO_3$, to form calcium oxide, commonly called burnt lime.

  $CaCO_3 \rightarrow CaO + CO_2$

- Calcium carbonate will react with water that is saturated with carbon dioxide to form the soluble calcium bicarbonate.

  $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

- This reaction is important in the erosion of carbonate rocks for forming caverns, and leads to hard water in many regions.

2.8.4 Commercial Uses of Precipitated Calcium Carbonate

Precipitated calcium carbonate is one of the most versatile mineral fillers and consumes in a wide range of products including paper, paint, plastic, rubber, ink, textiles, caulks, sealants adhesives etc. USP grades are used in dentifrices, cosmetics, foods and pharmaceuticals[10].

Plastics

- As a filler in rigid and plasticized PVC to improve impact strength
- As a filler in PVC footwear, wire and cable compounds/PVC film to improve surface gloss and other physical properties
- As a filler in synthetic leather- cloth/sheeting

Rubber

- As a reinforcing filler in natural and synthetic rubber for tyre and tube application
- As a filler for hawai chappals/soles/straps to improve the strength as well as whiteness

Surface Coatings

- In emulsion paints as a white opacifying agent
- As an anti-setting agent in paints
- In printing inks as an extender assisting in the control strength and body of the ink
- As a polishing agent in the window and mirror cleaners and polishes
- In powder coatings

Paper

The largest use of precipitated calcium carbonate is in the paper industry. In U.S.A, paper industry consumed about 75% of the total production.

- In paper coating for brightness, smoothness, opacity and ink receptivity
- In cigarette paper for control of opacity and burning rate
- As cost effective filler in alkaline sized papers giving high brightness and opacity

Pharmaceuticals

- As a calcium source
- As an antacid
- As a neutralization and filtration aid in antibiotic manufacture
- As a buffering and dissolution aid in soluble tabletting

Cosmetics

- In talcum powder to increase fulliness and control absorption characteristics
- In depilatory creams
- In face powders as a perfume carrier
- In sunscreen preparations

Dentifrices

- In powder and pastes as a polishing and cleaning agent

Food and Beverages

- In chewing gum
- As a calcium supplement
- In effervescent powder drinks
- To neutralize excess acid in food and wine manufacture
- As a filtration aid

Sealants and Mastics

- In PVC plastisols as rheology modifier particularly for car underbody
- Sealant applications on polyurethane, polysulfide, and silicone
- Sealants for construction and insulation glass applications as rheology modifier giving slump control

2.8.5 Production Process of Powder Calcium Carbonate

Powder calcium carbonate is produced by either chemical methods or by the mechanical treatment of the natural materials[3].

2.8.5.1 Mechanical Treatment of the Natural Materials

In this process good quality limestone are grounded for manufacturing calcium carbonate. The limestone used to make natural calcium carbonate must be carefully selected to assure good color and a minimum of metallic or abrasive impurities. In some instances physical or chemical beneficiation or both is used to upgrade the feed stone for the grinding mills[2]. The processes for making natural calcium carbonate suitable for paper coating are shown in Figure 2.15.

The finest products either the wet or dry system are 99.5% finer than 15 micron with a mean particle size of approximately 2.5 micron. The US paper coating industry refers to this product as fine-ground limestone (FGL). Two other grades intermediate fine ground limestone (IFGL) and ultrafine-ground limestone (UFGL) are also sometimes referred. Both of these products require more intense grinding than does FGL[2].

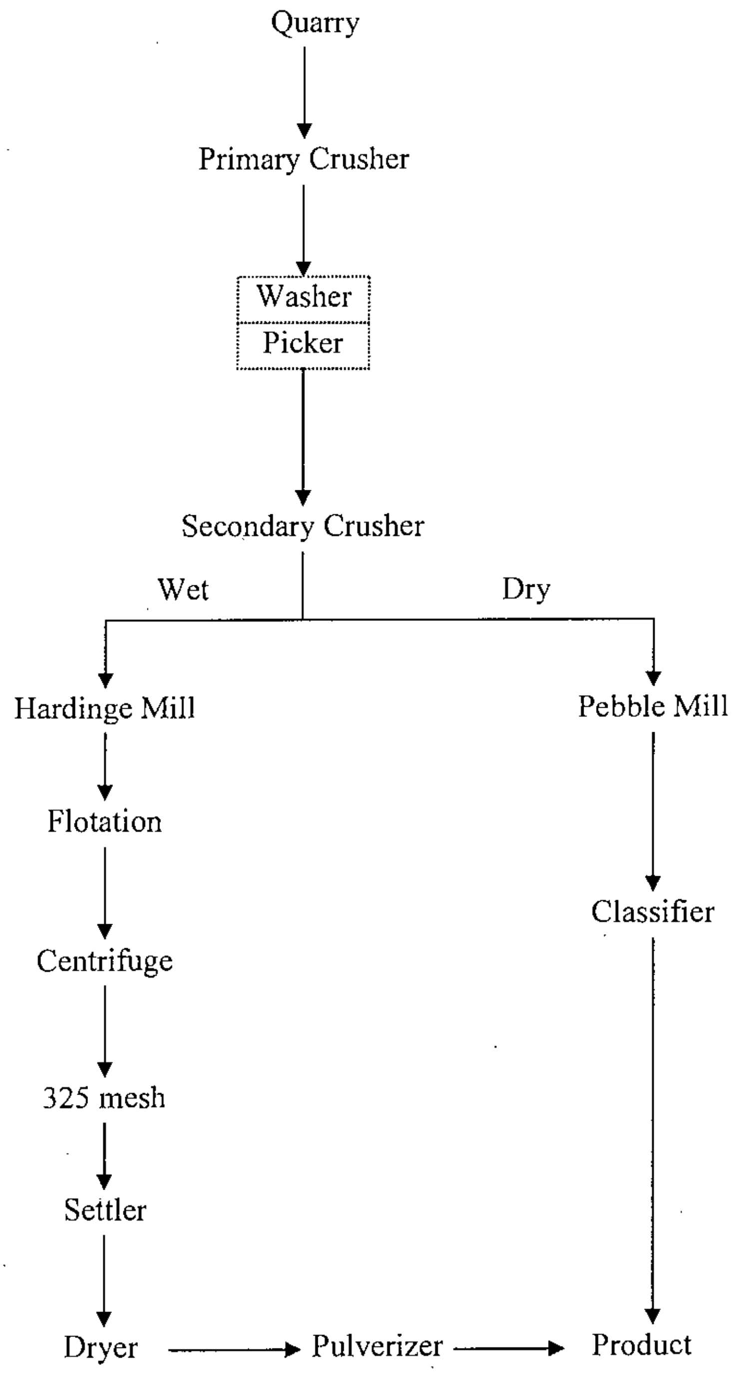


Figure 2.15: Production of powder limestone by mechanical treatment[2].

2.8.5.2 Chemical Methods (Precipitation Methods)

Precipitate Calcium carbonate can be produced by several methods such as[2]:

i. Carbonation Method

ii. Calcium Chloride-Sodium Carbonate Double Decomposition Method

iii. Lime-Soda Method

i Carbonation Method

Limestone is calcined in a kiln to obtain carbon dioxide and quicklime. Generally, these products are purified separately before recombining. The quicklime is mixed with water to produce either a milk of lime or dry hydrated lime; both are essentially all calcium hydroxide. When dry hydrate is used in the process, water is added to produce milk of lime slurry. Figure 2.16 shows production process of precipitated calcium carbonate by carbonation process[3].

In the carbonation process, the cooled and purified carbon dioxide bearing kiln gas is bubbled through the milk of lime in a reactor known as a carbonator. Gassing continues until all calcium hydroxide has been converted to the carbonate. The end point can be monitored by pH or by chemical measurements[3]. The reactions involved in this production method are:

Calcination: $CaCO_3 + \text{Heat} \longrightarrow CaO + CO_2$

Slaking: $CaO + H_2O \longrightarrow Ca(OH)_2$

Carbonation: $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

Reaction conditions determine the type of crystal, size of particles, and the size distribution produced. The process variables include[3]:

- starting temperature
- temperature during carbonation
- rate of mixing
- pH
- concentration of reactants
- pressure
- absence of chemical additives

Following carbonation the product can be further purified by screening as the impurities in the milk of lime remains as coarse particles in comparison to the micrometer sized, precipitated calcium carbonate. This screening, also used to control the maximum size of the product, is followed by dewatering. Rotary vacuum filters, pressure filters or centrifuges are used in mechanical removal of water. Washing of the filter cake is unnecessary as water is the only byproduct of carbonation. The filter cake solids are generally 25-60% $CaCO_3$, depending, to a large degree, on the particle size of precipitated calcium carbonate. Final drying is accomplished in either rotary film, tunnel, spray or flash dryer. This dried product is usually disintegrated in a micropulverizer. The milled material is conveyed to large storage bins for bulk loading or packing in bags.

Some coated grades are available for special applications. The precipitated calcium carbonate is coated to improve flow properties, processing, and physical properties of final products. Fatty acids, resins, and wetting agents used as coating materials are applied before or after drying[3].

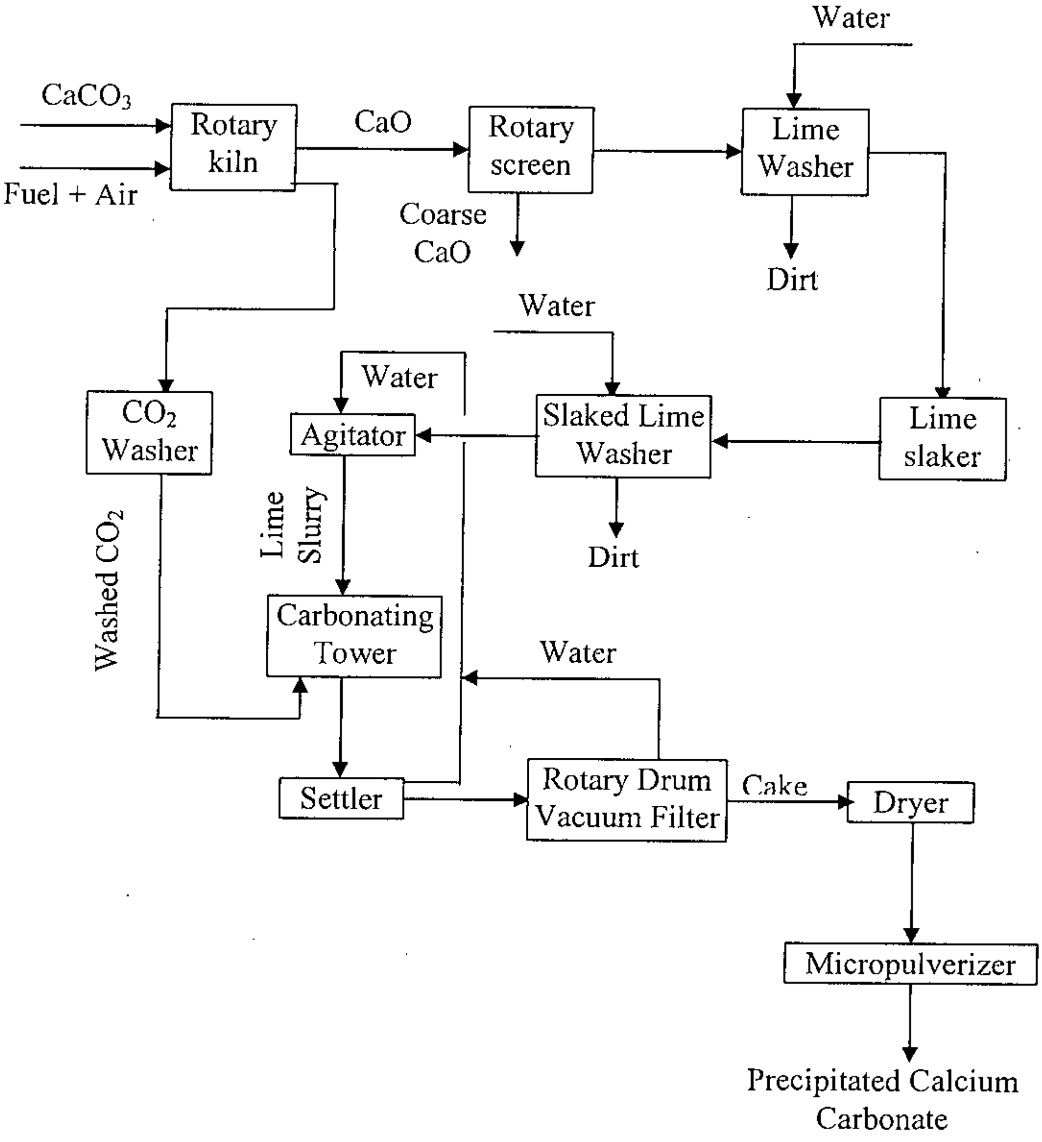


Figure 2.16: Production of precipitated calcium carbonate by carbonation process[3]

Recently Crescent Chemicals has set up a plant for production of precipitated calcium carbonate near Dhaka. Block diagram of this plant is shown in Figure 2.17.

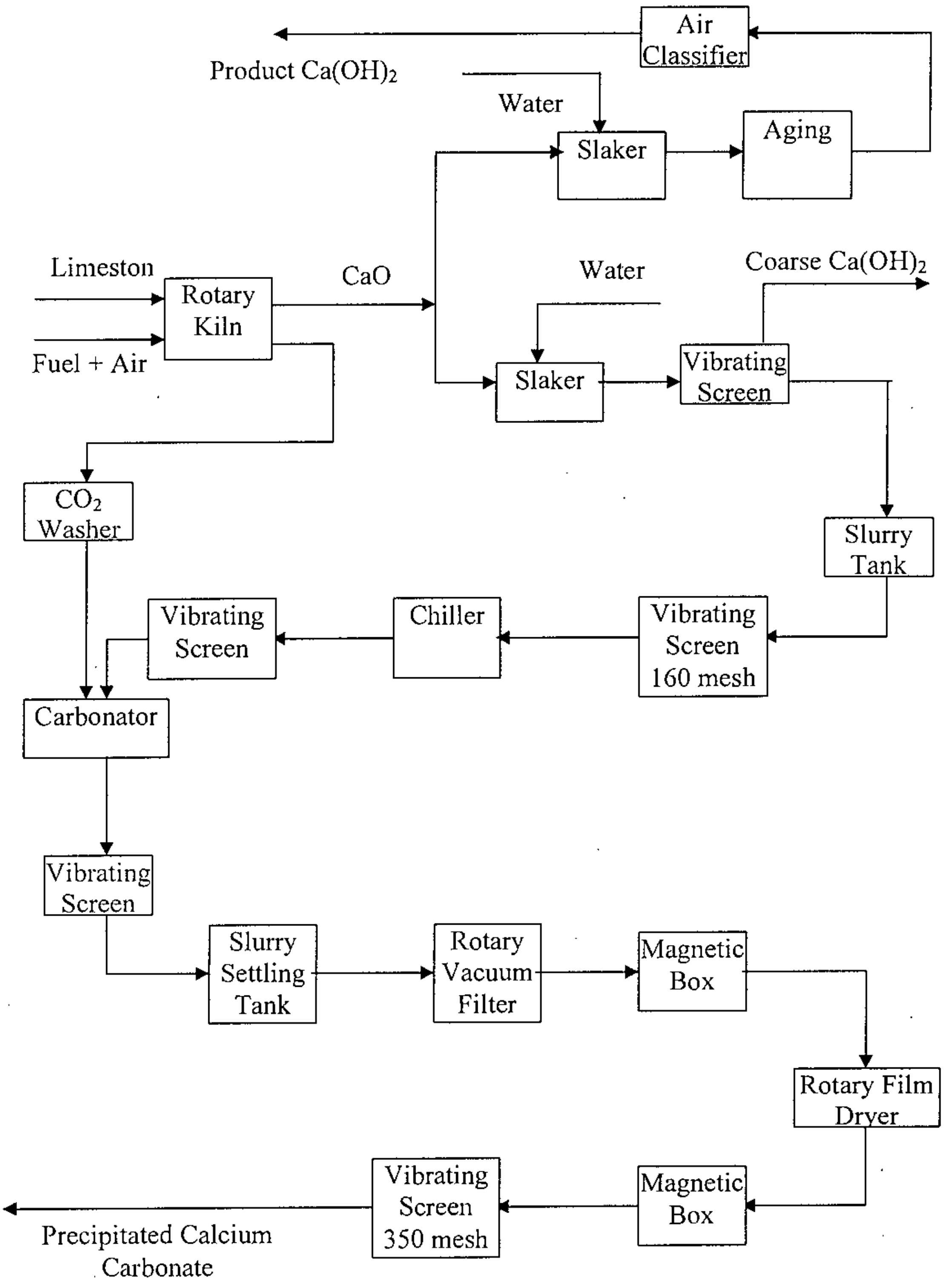


Figure 2.17: Carbonation process of producing precipitated calcium carbonate at Crescent Chemicals[10]

ii Calcium Chloride-Sodium Carbonate Double Decomposition Method

Prior to 1977, a significant quantity of the precipitated calcium carbonate was produced by manufacture of synthetic soda ash. A solution of soda ash reacts with a solution of purified calcium chloride yielding calcium carbonate and a sodium chloride byproduct. Figure 2.18 shows the block diagram of the process. The reaction is:

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$$

The process operating variables are:

- times
- rate and method of agitation
- concentrations
- pH
- reaction temperature

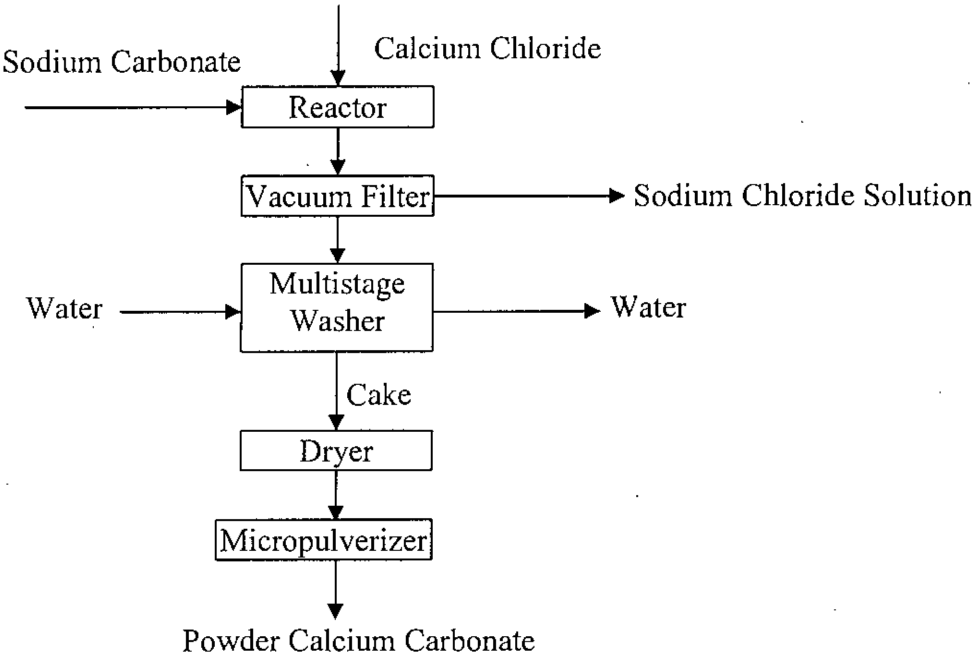


Figure 2.18: Production of calcium carbonate by calcium chloride-sodium carbonate double decomposition method

It is the simplest of the three processes but requires a low cost source of calcium chloride to be economically attractive. Commercial plants are located adjacent to Solvay process synthetic ash facilities. The sodium chloride was difficult to wash from carbonate filter cake and to remove in waste treatment facilities[3].

2.9 Separation Technique of Sodium Carbonate from Sodium Hydroxide

The lye from strong liquor storage tank is concentrated in multiple-effect evaporators having two or three stages. Because of elevation of boiling points, as the caustic liquors become more and more concentrated, the temperature difference between the steam side and the liquor side in each effect is limited. Steel or copper may be used as tube material up to concentration of 50%. Above 50%, nikel, inconel, monel etc. materials should be selected as tube metal in the evaporator. From freezing point curve Figure 2.3 of sodium hydroxide, it is clear that at concentration range 44-50%, corresponding freezing point is about 15^0C. At this concentration and temperature, sodium carbonate is sparingly soluble in the sodium hydroxide liquor. The hot strong caustic from the evaporator is drawn out into a tall cast iron tank in which it is allowed to settle. The separation of sodium carbonate is aided by cooling. If the solution is allowed to cool to 15^0C, sodium carbonate form crystals and can be separated from the bottom of the tank; but further cooling of solution makes sodium hydroxide too viscous, which retards the settling of sodium carbonate. An effective cooling and separation process reduces the sodium carbonate content in 50% caustic solution only below 0.5% at 30^0C yielding a high grade caustic for fusion or further evaporation to produce solid sodium hydroxide[1].

CHAPTER 3

STATEMENT OF THE OBJECTIVES

The liquid caustic soda produced by lime soda process contains appreciable amount of unreacted sodium carbonate. The byproduct calcium carbonate is also impure and cannot be used as such.

This work aims at studying the enhancement of yield of caustic soda in causticization reaction and encompasses the followings:

- carrying out reaction in several steps for exhausting one of the reactants to maximize yield in each step
- separation of unreacted sodium carbonate and caustic soda from precipitated calcium carbonate
- production of pure calcium carbonate to the maximum extent possible

Methodology followed to achieve above objectives includes:

i. Reaction was carried out under established operating conditions using both analytical and commercial grade reagents to make sodium hydroxide in several steps.
ii. Analysis of products by standard analytical methods.
iii. A scheme for recovery of caustic solution and at the same time removal of alkalinity of calcium carbonate powder.
iv. Recycling of the caustic solution (wash liquors) to the process to improve the yield.
v. Recovering precipitated calcium carbonate.

CHAPTER-4

EXPERIMENTAL WORK

4.1 Introduction

Causticization was carried out in the laboratory by using analytical and commercial grades of lime and sodium carbonate as reactants. Before performing causticization reaction, calcium oxide and soda ash were analyzed (**Appendix- A1:** Analytical procedures and **Appendix-D:** Analysis). A series of batch reactions were performed keeping calcium oxide as limiting reactant in the first stage for each batch. In subsequent stages, sodium carbonate was the limiting reactant by having excess calcium oxide. Some batches were carried out in three stages and the others were in two stages. The two stage batch process was selected because overall conversion was same for each batch whether in two stages or three stages. Detailed observed data, calculated data and sample calculation are shown in **Appendix-A.**

4.2 Description of the Experimental Set-up

The main equipment of carrying out lime-soda process to prepare caustic soda are the glass causticizer and vacuum filter.

4.2.1 Causticizer

A two-liter three necked round bottom heat resistant glass flask (Durane, German) was used as causticizer. The size of the central neck was 45/40 mm and the other two side necks were 32/29 mm. The stirrer was fitted through the central neck of the flask and was driven by an electric motor. It was used to keep calcium hydroxide in suspension by agitation. The other two necks were used to place condenser and thermocouple. Rubber stoppers with holes drilled through their center for installing stirrer, condenser and thermocouple were placed on the necks. The causticizer was thus made vapor-leak proof. Figure 4.1(a) shows the causticization system used schematically and Figure 4.1(b) is the photograph of the experimental causticizer used.

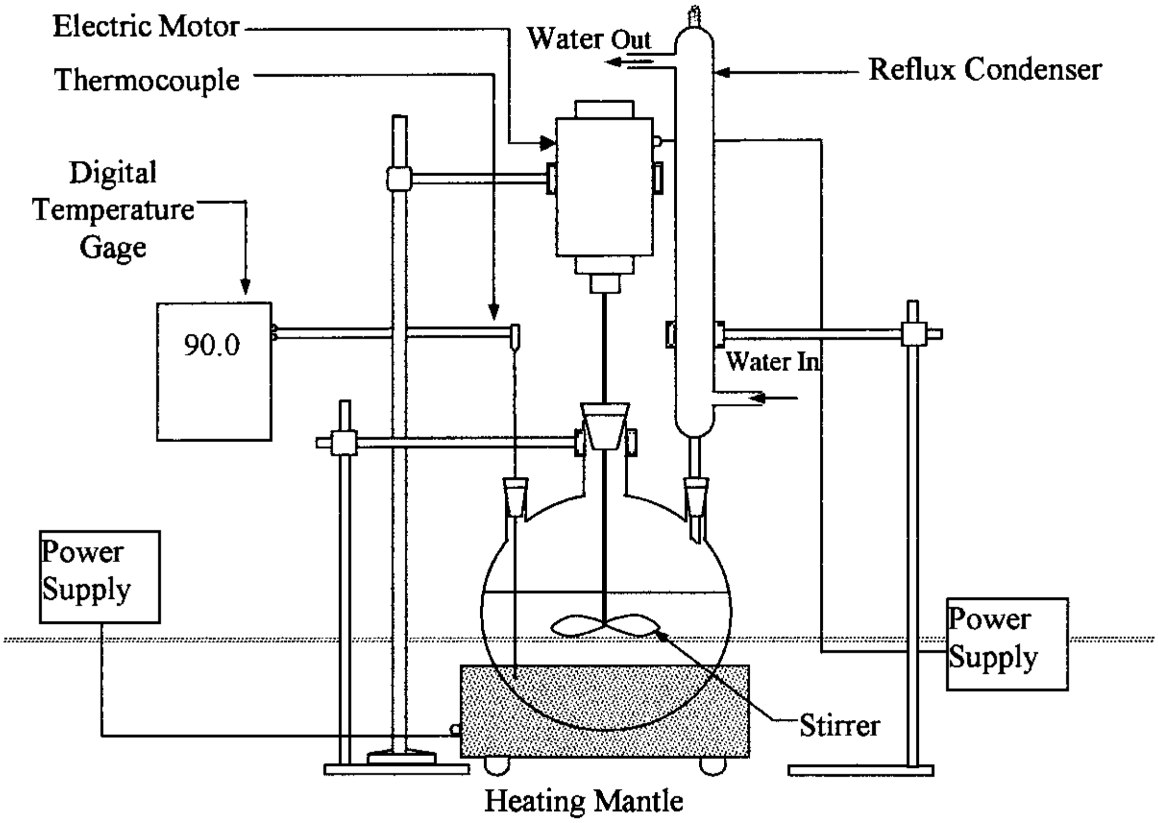


Figure 4.1(a): Schematic diagram of causticization set-up

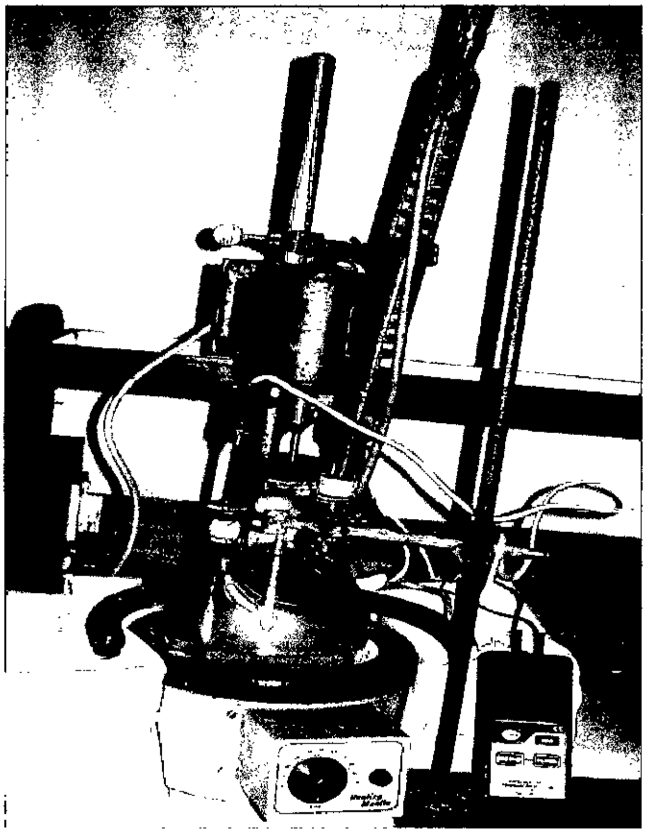


Figure 4.1(b): Photograph of causticization set-up

4.2.2 Vacuum Filter

This unit consists of a vacuum pump, filtrate collecting conical flask, filter media and funnel. Whatman-41 filter paper was used as filter. Vacuum pump was used to create vacuum in the unit. The main function of the vacuum pump was to create driving force for flow through the filter paper and this increased the rate of filtration. Figure 4.2(a) shows the schematic diagram of vacuum filtration system used and Figure 4.2(b) is the photograph of vacuum filtration used.

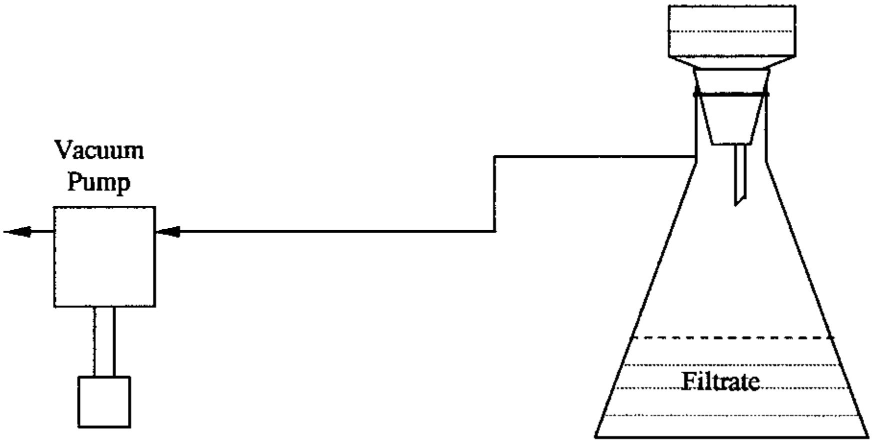


Figure 4.2(a): Schematic diagram of vacuum filtration

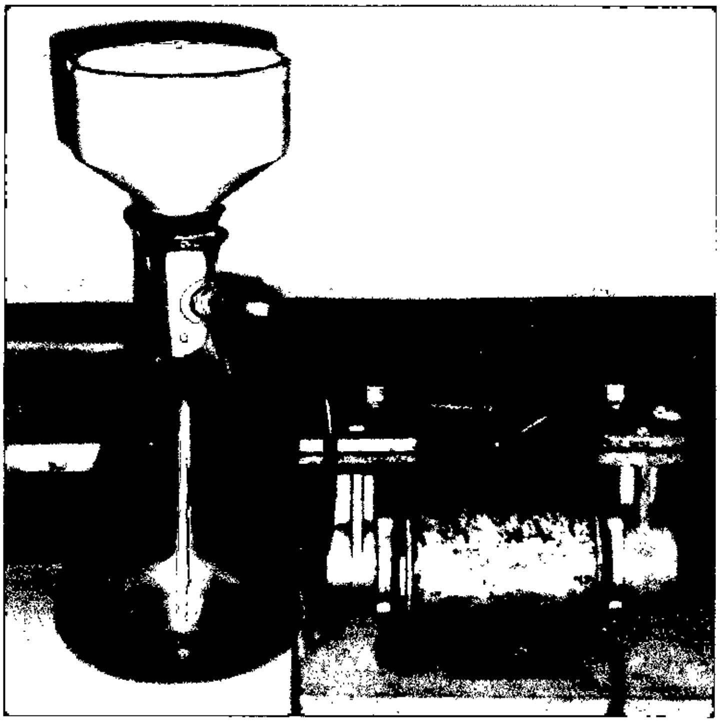


Figure 4.2(b): Photograph of vacuum filtration

4.2.3 Product and Recovered Solution Storages

Beakers were used to store products and recovered caustic soda from byproduct calcium carbonate after multistage washing. Figure 4.3 shows the storages of products and recovered caustic soda from different washing stages.

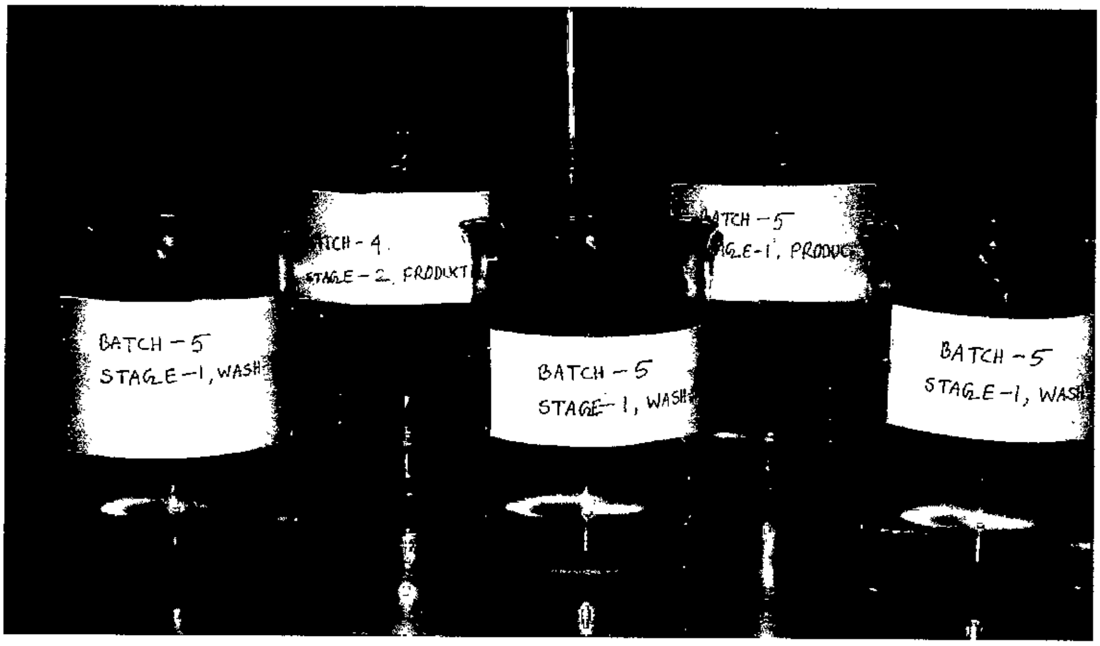


Figure 4.3: Storages of product and recovered caustic soda

4.2.4 Dryer

An electric oven with tray was used to dry byproduct calcium carbonate. The temperature of the dryer was controlled automatically.

4.3 Description of the Laboratory Work

In the initial phase of this work, causticization was carried out in three stages using reagent grade reactants. Four batches of three stage causticization were performed. In the first stage, only percentage of stoichiometric lime charged in the causticizer was varied from batch to batch. In the second stage, 95% of stoichiometric lime was added for each batch. Finally in the third stage, fifty percent excess lime was charged in causticizer to carry out causticization. For two stage causticization, first stage was carried out keeping lime at 90% of its stoichiometric amount while the second stage was performed with 50% excess lime. The outcomes of these two types of batch were compared and finally two stage causticization was selected. Thus the later experiments of causticization for both analytical and commercial grade reactants were performed in two stages. Established data for two stage causticization reaction with recycle were found out. Detailed observed and calculated data are shown in **Appendix-A3**. In the initial batch 12.5% sodium carbonate solution was prepared by taking 105 g available soda ash in 735 ml water in a beaker. For subsequent batches the first washed solution of both stage obtained from this batch was recycled and fresh sodium carbonate was added into the recycle stream as makeup. The amount of calcium oxide was charged as described earlier. The whole experimental work for a stage was done by following steps.

4.3.1 Causticization

The causticization setup has been described already. The reactants were charged through the neck fitted with thermocouple by taking it out. Cooling water was supplied to condenser. The causticizer was sealed (using stirrer, condenser, thermocouple in three neck) and the stirrer was then switched on. Heating of solution was started by keeping switch on of electro mantle to raise the temperature of the solution at 90^{0}C. After reaching the temperature at 90^{0}C, it was maintained for 2.5 hrs. The pressure in the causticizer was maintained at atmospheric pressure by keeping the top of condenser open. After causticization for the stipulated time, the stirrer and heating mantle were switched off and the stirrer, thermocouple and condenser were removed from the flask and the valve for condenser cooling water was closed. The slurry was then poured into a beaker for settling and filtration. Figure 4.4 shows the block diagram of two stage causticization carried out in the laboratory.

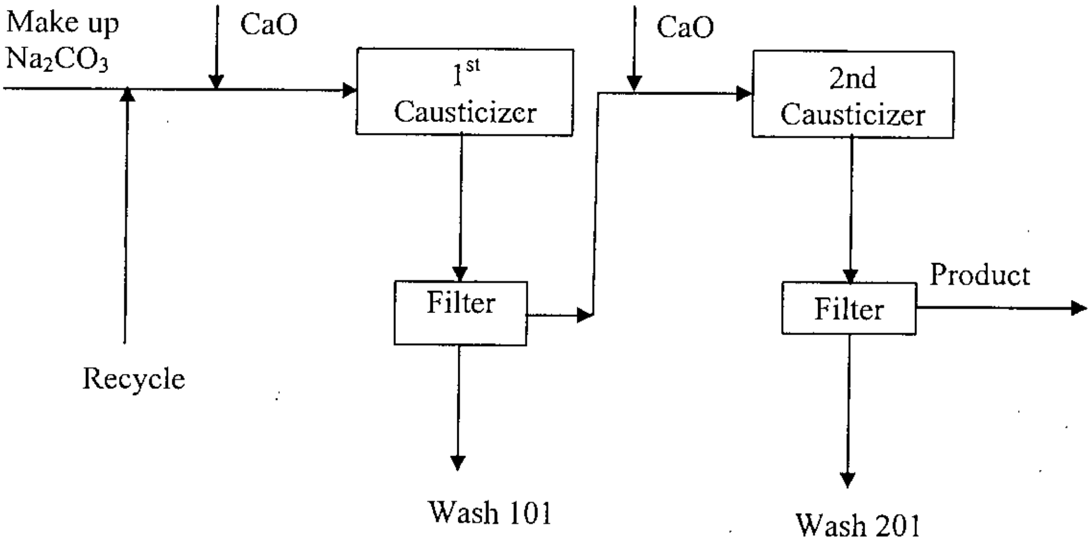


Figure 4.4: Block diagram of two stage causticization carried out in the laboratory

4.3.2 Filtration

After completion of the settling of the slurry, the clear solution was decanted and the thick dense slurry was sent to vacuum filtration to separate caustic solution from calcium carbonate precipitate. For each stage, filtration was carried out four times; one for separating product liquor from calcium carbonate precipitate and the other three for washing of precipitated calcium carbonate cake to recover caustic soda and soda ash.

4.3.3 Analysis of Filtrate

Titrations were performed to find out amount of sodium carbonate and sodium hydroxide present in the filtrate. After each filtration, the filtrate was collected in a beaker and stored. 10 ml sample volume was taken and titrated against standard hydrochloric acid using phenolphthalein and methyl orange double indicator. The first end point was the volume of hydrochloric acid required to neutralize OH^- and to convert CO_3^{--} to HCO_3^-. The second end point determined the volume of hydrochloric acid required to break HCO_3^- to CO_2 which was the final point of titration. The procedures are given in **Appendix-A1**.

4.3.4 Caustic Recovery

Calcium carbonate cake contains a substantial amount of caustic soda in its pore space. To recover caustic soda from calcium carbonate, it was washed thrice. Figure 4.5 shows block diagram for washing of precipitated calcium carbonate for two-stage causticization batch. For the first stage of first batch, fresh water was used in each washing stage. The second washed solution from first stage was used to wash the cake for first wash for the second stage of the same batch. The third washed solution was sent to second wash in the second stage of the same batch and used as first washing solution in the first stage of the next batch and so on. For third washing in stage two, fresh water was used and sent to second washing for the first stage and first washing for the second stage of the next batch and so on. Thus caustic from calcium carbonate was recovered and used as recycle stream.

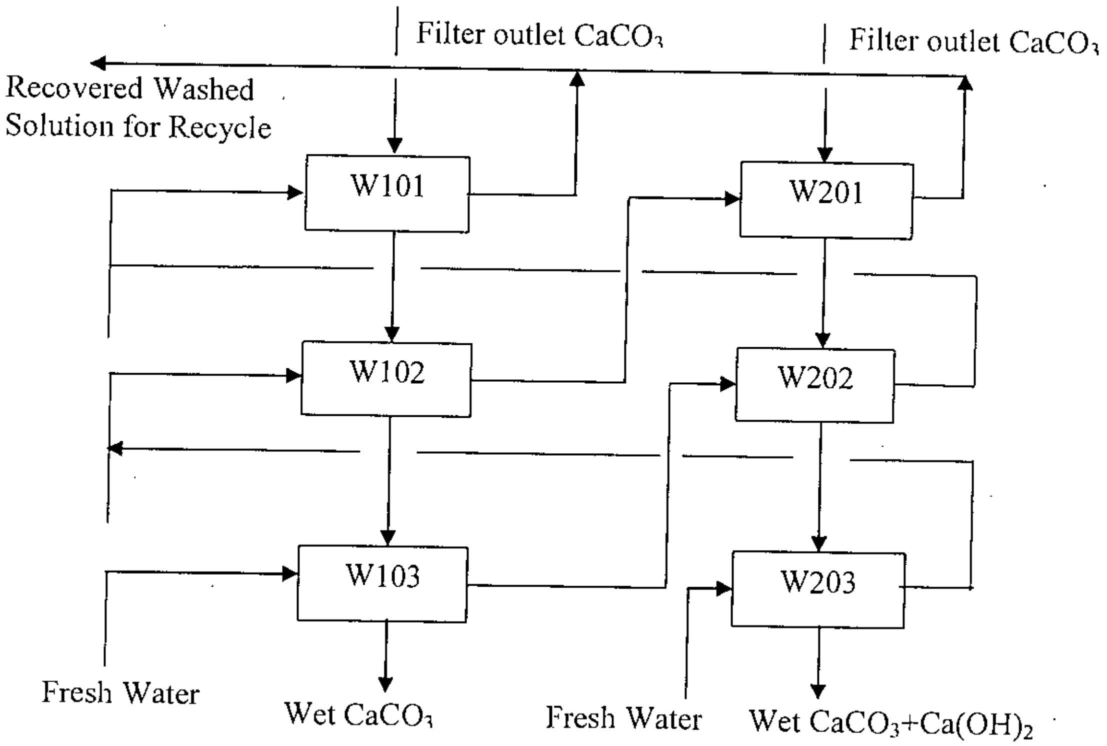


Figure 4.5: Block diagram for washing methodology used to wash precipitated calcium carbonate for two-stage causticization batch

4.3.5 Drying of Calcium Carbonate

The cake deposited on the filter paper from last washing stage was dried in an electric oven. Initially cake was placed on tray with filter paper. The temperature of dryer was set at 100^{0}C and the cake was kept at this condition about an hour. After then the filter paper was removed from cake and it was disintegrated manually. The cake was dried for several hours keeping temperature set at 110^{0}C.

The laboratory work undertaken to complete the causticization in a batch is schematically shown in Figure 4.6.

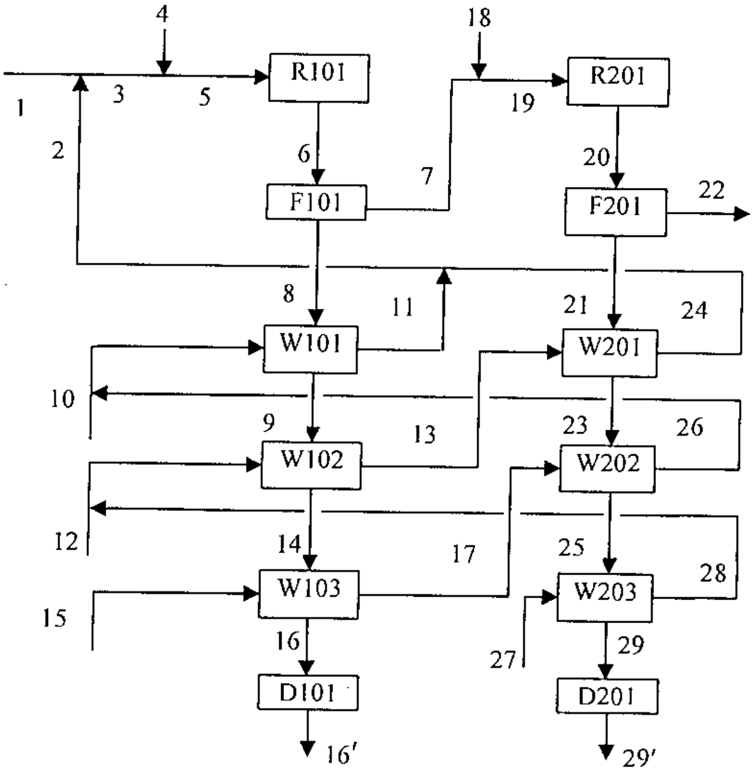


Figure 4.6: Block diagram for experimental setup performed in the laboratory to carry out causticization reaction in two-stage.

Nomenclature of Block Diagram

1: Fresh sodium carbonate feed to reactor
2: Recycle caustic solution from previous batch
4: Lime feed to reactor (90% of stoichiometric amount)
5: Total reactants to first causticizer
6: Total effluent from first causticizer
7: First stage product caustic solution
8: Byproduct calcium carbonate
9: First washed calcium carbonate
10 (26): Second washed solution from second stage of previous batch
11: First washed solution from stage 1 used as recycle stream for next batch
12 (28): Third washed solution from second stage of previous batch
13: Second washed solution from first stage
14: Second washed calcium carbonate
15: Fresh water feed to system
16: Washed calcium carbonate
16′: Dried calcium carbonate
17: Third washed solution from first stage
18: Lime feed to second causticizer
20: Total effluent from second causticizer
22: Product sodium hydroxide from second stage
24: First washed solution from stage 2 used as recycle stream for next batch
27: Fresh water feed to system
29: Washed calcium carbonate and unreacted lime
29′: Dried calcium carbonate and unreacted lime
R101: First causticizer
F101: First causticizer outlet filter
W101: First calcium carbonate washer after first causticizer
D101: First stage outlet calcium carbonate dryer
R201: Second stage causticizer
F201: Second stage outlet filter
W201: Second stage outlet calcium carbonate first washer
D201: Second stage outlet calcium carbonate dryer

CHAPTER - 5

RESULTS

5.1 Product Sodium Hydroxide

The causticization reaction was carried out using analytical and commercial grades of soda ash and lime. To find out the optimum number of stages, initially some experiments consisting three and two stages were performed using analytical grade reactants. The results of these experiments are shown in Table 5.1 and Table 5.2. The detailed observed and calculated data are shown in **Appendix- A3**.

Table 5.1: Comparison between initial three and two stage batches

Composition of Product NaOH	Percent by Weight	
	Two Stage	Three Stage
Sodium Hydroxide	9.20-9.70	10.20-10.70
Sodium Carbonate	0.78-0.86	1.04-1.10
Water	90.00	89.00
Overall conversion based on Na_2CO_3	92.1-93.2%	91.3-93.2%

Table 5.2: Summary of conversion and recovery of initial three and two stage batches

Batch No.	Stage No.	% Conversion		% Overall Conversion	% Recovery of Equivalent Na_2CO_3	
		Basis: CaO	Basis: Na_2CO_3	Basis: Na_2CO_3	Each Stage	Overall
1	1	94.40	67.14	91.25	98.90	96.70
	2	72.00	73.50		98.62	
	3	20.65	31.18		98.90	
2	1	96.50	73.15	92.80	99.24	97.80
	2	81.35	79.30		98.62	
	3	7.10	15.90		99.60	
3	1	95.28	74.16	93.20	99.20	97.92
	2	68.40	67.86		98.99	
	3	12.77	19.50		99.60	
4	1	93.90	76.15	91.89	99.20	95.40
	2	43.40	48.07		98.64	
	3	22.65	52.52		97.88	
5	1	95.30	87.50	93.20	99.00	98.20
	2	31.10	50.74		99.50	
6	1	93.00	86.60	92.10	97.70	95.90
	2	18.10	55.14		98.00	
7	1	95.00	87.44	93.20	99.90	99.80
	2	32.50	49.39		99.89	

Table 5.1 provides a comparison based on the composition of product sodium hydroxide and overall conversion based on sodium carbonate, while Table 5.2 provides conversions based on calcium oxide, sodium carbonate, overall conversion based on sodium carbonate and recovery of equivalent sodium carbonate for different stages for three stage and two stage causticization reactions.

The overall conversion in three and two stage causticization was same and it was no more than 93.2% based on Na_2CO_3. Purity of sodium hydroxide gets worsened with three stages with increased presence of sodium carbonate. Since the overall conversion for three and two stage causticization is same, two stage causticization was selected for further studies.

Two stage causticization was performed using both commercial and analytical grade reactants. Table 5.3 shows summary of percentage conversion and recovery for analytical grade reactants. The conversions of sodium carbonate and calcium oxide from first stage are 85.64-86.72% and 94.8-95.2%. The overall conversion of sodium carbonate is 92.9-94%. Table 5.4 shows summary of percentage conversion and recovery for commercial grade reactants. The conversions of sodium carbonate and calcium oxide from first stage are 87.6-88.1% and 97-97.5%. The overall conversion of sodium carbonate is 93.2-94.2%.

Table 5.3: Summary of conversion and recovery of two stage causticization for analytical grade reactants

Batch No.	Stage No	% Conversion		% Overall Conversion	% Recovery of Equivalent Na_2CO_3	
		Basis: CaO	Basis: Na_2CO_3	Basis: Na_2CO_3	Each Stage	Overall
8	1	95.16	86.72	92.90	99.90	99.73
	2	35.84	55.27		99.80	
9	1	94.79	85.75	94.00	99.63	99.50
	2	32.58	49.83		99.90	
10	1	95.00	85.68	93.90	99.86	99.63
	2	31.66	47.50		99.80	
11	1	95.02	85.67	93.96	99.87	99.70
	2	32.00	49.00		99.87	
12	1	95.13	85.64	93.93	99.90	99.80
	2	32.33	48.96		99.90	
13	1	95.05	85.70	93.96	99.86	99.75
	2	32.31	48.96		99.94	

Table 5.4: Summary of conversion and recovery of two stage causticization for commercial grade reactants

Batch No.	Stage No	% Conversion		% Overall Conversion	% Recovery of Equivalent Na_2CO_3	
		Basis: CaO	Basis: Na_2CO_3	Basis: Na_2CO_3	Each Stage	Overall
1	1	97.04	87.60	93.24	99.70	99.60
	2	30.50	49.95		99.90	
2	1	97.26	87.85	94.15	99.70	99.51
	2	26.27	38.04		99.85	
3	1	97.50	88.10	94.00	99.80	99.63
	2	23.20	35.63		99.90	
4	1	97.45	87.82	93.95	99.70	99.45
	2	22.10	34.50		99.87	
5	1	97.46	87.80	93.90	99.70	99.45
	2	21.50	33.68		99.87	

5.2 Byproduct Calcium Carbonate

The byproduct from causticization process is calcium carbonate which is also a useful industrial chemical. The byproduct calcium carbonate produced in this process was analyzed in the laboratory at Crescent Chemicals Ltd., Gazipur. Table 5.5 lists various measured parameters that determine the quality of calcium carbonate. Analytical procedures are given in **Appendix -A1.**

Table 5.5: Analytical results of precipitated calcium carbonate produced by lime-soda process

Name of Test	Analytical Grade Reactants	Commercial Grade Reactants
Calcium Carbonate, %	98.30	96.67
Calcium Oxide, %	1.22	1.27
Iron (Fe), ppm	468	1073
Bulk Density, g/ml	0.784	0.579
Settle Volume, ml/min	8/25	13/25
Moisture, %	0.40	0.24
Color	Bright White	White

The byproduct calcium carbonate as well as commercial precipitated calcium carbonate (Crescent Chemicals Product) was also analyzed in the laboratory. Table 5.6 shows these results. Crystal structures were determined by chemical method. The crystal structure of each product was found calcite. Calcite crystal structure was also observed by Scanning Electron Microscope (SEM) method. Figure 5.1-5.3 shows the Scanning Electron

Microscopic view of calcite structure. Figure 5.4 shows the photograph of precipitated calcium carbonate produced from commercial grade reactants.

Table 5.6: Analytical results of precipitated calcium carbonate in the laboratory

Name of Test	Analytical Grade Reactants	Commercial Grade Reactants	Crescent Chemicals Product
Calcium Carbonate, %	98.3-99	96.2-97	97.06
Calcium Oxide, %	0.2-0.4	0.3-0.4	0.375
Crystal Structure	Calcite	Calcite	Calcite

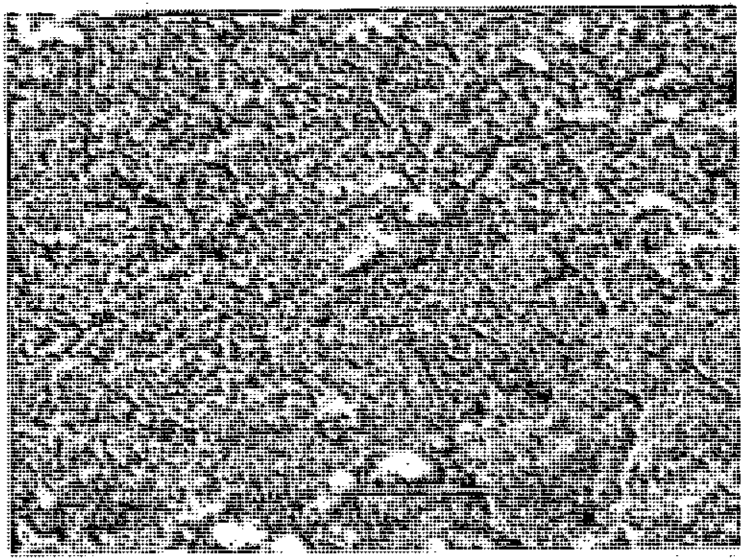


Figure 5.1: Crystal structure of precipitated calcium carbonate by SEM method (Crescent Chemicals Product -calcite)

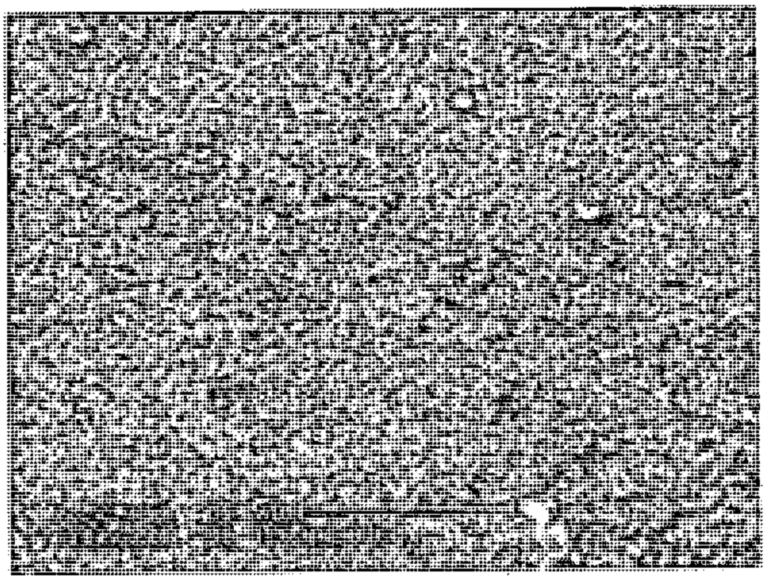


Figure 5.2: Crystal structure of precipitated calcium carbonate by SEM method (analytical grade reactants-calcite)

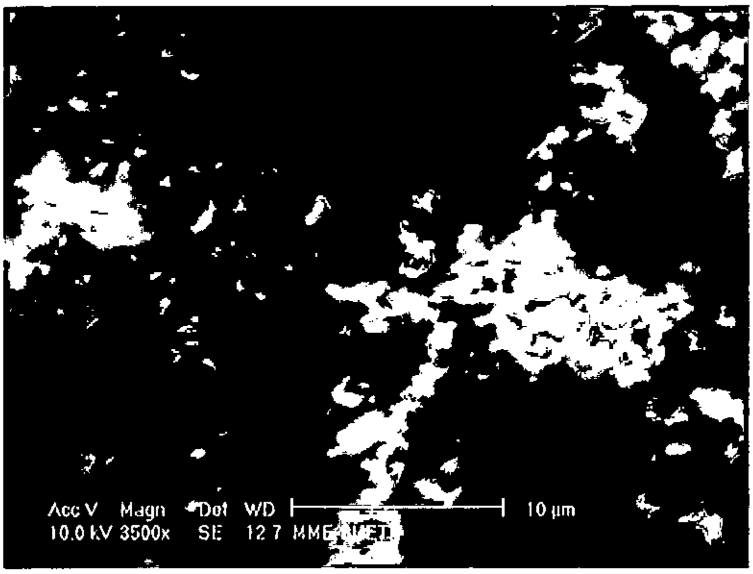


Figure 5.3: Crystal structure of precipitated calcium carbonate by SEM method (commercial grade reactants-calcite)

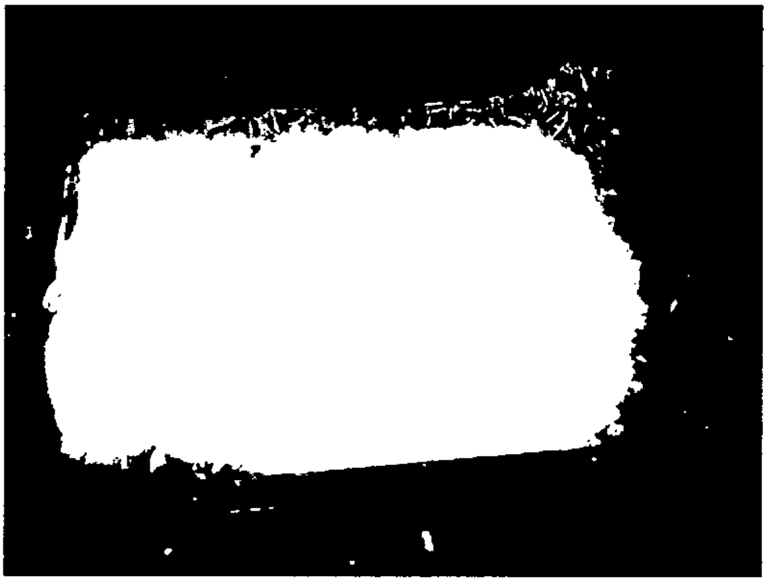


Figure 5.4: Photograph of precipitated calcium carbonate (commercial grade reactants)

CHAPTER - 6

DISCUSSION

The main challenge of this work was to enhance conversion of sodium carbonate by adopting multi-stage operation. Since literature is available only for single stage causticization of sodium carbonate with excess lime. The conversion of soda ash depends on initial concentration of sodium carbonate, properties of lime, temperature etc. The equilibrium conversion curve, Figure 2.8 shows effect of concentration on conversion of sodium carbonate. It is clear from this Figure that the conversion will not be more than 93-94% if the causticization reaction is carried with 12.5% sodium carbonate solution. At this conversion there exists equilibrium between carbonate ion and hydroxyl ion. When equilibrium is attained between carbonate ion and hydroxyl ion, sodium carbonate does not go for any further conversion, even the causticization is continued without removal of calcium carbonate. The product sodium hydroxide from this process contains some unreacted sodium carbonate.

The equilibrium conversion for 12.5% sodium carbonate solution is about 94%. In practice it does not average much over 90% conversion in single stage causticization. Hence the first stage of causticization was carried out with 90% stoichiometric amount lime. The purpose of performing this stage was to get 100% conversion of lime i.e., to get high quality precipitated calcium carbonate. In the case of commercial grade reactants dry calcium hydroxide and sodium carbonate were used to carry out causticization and the conversion from first stage was about 97.5%, but that for analytical grade was about 95%. The reagent grade quick lime used was from an old stock. The exact physical state of the lime is unknown. What has led to conversion lower than expected (calculated) is difficult to explain. But the overall conversion found from each grade was about 94%, remained same for each type of reagent.

Mannan, 1998[9], performed causticization process in one stage in the laboratory with 12.5% initial sodium carbonate solution. Conversion from this process was 92.1% based on sodium carbonate. But the calculation procedure was wrong and actual conversion would be 84.4%. Again he did not give any information about byproduct calcium carbonate. One stage wash of calcium carbonate with 500 ml water was done to recover caustic soda from this calcium carbonate. The percentage recovery from this process was 96.45%.

Imtiaz, 1999[8], also carried out causticizing reaction in the laboratory and the overall conversion was about 92.4% based on sodium carbonate. He performed a detailed study of recovery of caustic soda from precipitated calcium carbonate and drying of this precipitated calcium carbonate. The causticizing reaction was carried out in one stage with 10% excess calcium hydroxide. After causticization, the sludge was separated by vacuum filtration. 150-200 ml water was added with this sludge and subjected to another causticization and the process was repeated for three times. Thus the process gives three dilute liquors of caustic soda with first stage product. The study did not give any idea about these three liquors. The recovery from the process was 85.1%. But the calculation procedure of percent of recovery from the process was not correct. The actual recovery from the process would be 87.55%. It was done only on the basis of recovered caustic soda. Unreacted sodium carbonate should have been included to find out recovery from causticization process. Table 6.1 shows summary of comparison among present two stage causticization process with previous works.

Table 6.1: Comparison of present work with previous one stage causticization process

Item	Mannan[9], One Stage	Imtiaz[8], One Stage	Present Work, Two Stage
Conversion Basis: Na_2CO_3	85.6%	92.4%	94.2%
Recovery based on Equivalent Na_2CO_3	96.45	87.55.	99.5%

The recovery from present study is about 99.5%. The implementation of current methodology of washing made this possible. The product calcium carbonate was subjected to three stages wash to recover caustic soda from it as described in Chapter 4. In this methodology only fresh water was added in the third washing stage, used three times as washing liquid, and finally recycled to process to prepare soda ash solution and lime slurry. This methodology of washing gives only one grade of caustic soda and also increases recovery. It drastically reduces alkalinity of calcium carbonate due to three stage washing.

The byproduct calcium carbonate was analyzed in the laboratory at Crescent Chemicals. Table 5.5 shows result of this analysis and Table 6.2 shows comparison among produced calcium carbonate by present study to commercial precipitated calcium carbonate produced at Crescent Chemicals Ltd. For analytical grade reactants, the calcium carbonate percent was found about 98.3%, and 96.67% for commercial grade reagents. The bulk density of product calcium carbonate obtained from this process was higher than the product obtained from carbonation process at Crescent Chemicals Ltd. Presence of Iron, settle volume, color, etc also affect quality of calcium carbonate.

Table 6.2: Comparison of laboratory produced $CaCO_3$ with commercial grade

Tests	This Work		Commercial $CaCO_3$ (Crescent Chemicals Ltd)
	Analytical Grade Reactants	Commercial Grade Reactants	
Calcium Carbonate, %	98.30	96.67	96.00
Calcium Oxide, %	1.22	1.27	0.12
Iron (Fe), ppm	468	1073	>1000
Bulk Density, g/ml	0.784	0.579	0.4-0.45
Settle Volume, ml/min	8/25	13/25	18/25
Moisture, %	0.40	0.24	0.50
Color	Bright White	White	White

The bulk density is very important criteria of precipitated calcium carbonate for consuming the product in paper, plastic, ceramic, rubber industries etc. The great problem of Crescent Chemicals is low bulk density of their product calcium carbonate. As a result they can not expand their market in those sectors like paper making industries where high bulk density is the prime requisite of precipitated calcium carbonate. The color of the product calcium carbonate was also white.

The byproduct precipitated calcium carbonate produced in this work and commercial precipitated calcium carbonate (Crescent Chemicals Ltd. product) were also analyzed in the laboratory. Table 5.6 shows results. For analytical grade reactants, the percent of calcium carbonate was found about 98.3-99%, and 96.2-97% for commercial grade reactants and that was about 97% for commercial precipitated calcium carbonate. The calcium oxide content was same for each grade of product.

Calcium carbonate occurs in nature either of two polymorphs: calcite or aragonite. The crystal form of calcite is hexagonal form and aragonite is in orthorhombic system. In the commercial forms of precipitated calcium carbonate, where aragonite predominates, crystals have parallel sides and large length to width ratios. The structure of the byproduct was analyzed in the laboratory by chemical method and by Scanning Electron Microscope method. The byproduct calcium carbonate was of calcite structure. Figure 5.1-5.3 shows the Scanning Electron Microscopic view of calcite structure. Figure 5.4 shows photograph of product precipitated calcium carbonate for commercial grade reactants. It indicates the whiteness of calcium carbonate.

There is no scope of building new caustic-chlorine plant in Bangladesh because the byproduct chlorine has little demand and that has been met already. Again the production of caustic soda from lime-soda process is not cost effective if it is produced using conventional one stage process. The conventional one stage process may be replaced by present two stage causticization method. In present lime-soda process, the byproduct calcium carbonate is highly pure, comparable with commercially available calcium carbonate. The byproduct calcium carbonate has a great demand in various industries as filler, coating, adhesive etc., so this two stage lime-soda process may play an important role in partial fulfilling the demand of caustic soda and calcium carbonate. Marketing of this quality byproduct calcium carbonate will improve the economic viability of lime-soda process in Bangladesh.

CHAPTER - 7

CONCLUSION

From the experimental work the following conclusion may be drawn

a) The conversion of sodium carbonate from first stage was 85.64-86.72% and 87.6-88.1 for analytical grade and commercial grade reactants respectively.

b) The overall conversion of sodium carbonate into sodium hydroxide in two stage causticization was about 93-94%, which was not possible using single stage only

c) Overall recovery of equivalent sodium carbonate from the process was about 99.5%.

d) The conversion of calcium oxide in the first stage has been calculated in two ways;
   i. product calcium carbonate basis: conversion was 97.8% for analytical and 97.7% for commercial grade reactants and
   ii. product sodium hydroxide basis: conversion was 95-95.2% for analytical grade reactants which was above 97.5% for commercial grade reagents.

e) The byproduct calcium carbonate obtained from the process was pure. The quality of the product was comparable with the commercially available precipitated calcium carbonate produced from carbonation method. In case of analytical grade reactants, the produced calcium carbonate was 98.3%, which was 96.67% for commercial grade reactants.

f) The precipitated calcium carbonate was calcite type.

CHAPTER – 8

RECOMMENDATION

The following works should be undertaken in future for the indigenous development of lime soda process:

- Quick lime is very hygroscopic in nature which absorbs moisture from environment. Before the start of each batch determination of percentage of calcium oxide is recommended.
- On the other hand causticization reaction can be carried out using dried slaked lime instead of quick lime in the laboratory. Because it has no tendency to absorb moisture from the environment.

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APPENDICES

APPENDIX- A

Appendix- A1

Analytical Procedure

Appendix- A1 Analytical Procedure

A.1.1 Analysis of Caustic Soda Solution

Introduction

The caustic soda solution produced from lime soda process is a mixture of NaOH and Na_2CO_3. This has been determined by titrating against standard hydrochloric acid using phenolphthalein and methyl orange double indicator method. At the phenolphthalein end point all the hydroxide is neutralized and the carbonate is converted into hydrogen-carbonate.

$$OH^- + H^+ = H_2O$$

$$CO_3^= + H^+ = HCO_3^-$$

Another titration is performed with methyl orange indicator. At the end point all the hydroxide and the carbonate are neutralized.

$$OH^- + H^+ = H_2O$$

$$CO_3^= + H^+ = HCO_3^-$$

$$HCO_3^- = H_2O + CO_2$$

Procedure:

i) 10 ml of caustic solution was transferred to a conical flask with a pipette

ii) 2-3 drops of phenolphthalein was added into the solution

iii) the solution was titrated against with 0.097 N HCl. Color changed from pink to colorless

iv) Another titration was done exactly following the above procedure with methyl orange indicator. Color changed from orange to faint pink

Sample calculation is shown in Appendix- A2

A.1.2 Determination of Sodium Carbonate Content in Soda Ash

The sodium carbonate content of soda ash was determined by titrating soda solution against standard hydrochloric acid.

Procedure

a) About 5.3 g of soda ash was weighted, dissolved in distilled water, and diluted it to 1000 ml in a volumetric flask.

b) 20 ml solution was taken in a conical flask, and titrated against standard 0.105 N hydrochloric acid using methyl orange as indicator. The color changed from orange to faint pink was the end point of titration.

Sample Calculation

Table A.1.1: Observed data for determination of sodium carbonate in soda ash

Experiment No.	Volume of Soda Ash Solution ml	Volume of HCl Required ml	Strength of HCl N
1	20	18.1	0.105
2	20	18.15	

Average volume of HCl, $V_1 = 18.125$ ml

Strength of HCl, $S_1 = 0.105$ N

Volume of Soda Ash Solution, $V_2 = 20$ ml

Strength of Soda Ash Solution, $S_2 = V_1 S_1 / V_2 = 18.125 \times 0.105 / 20 = 0.095$ N

1000 ml solution contains = $0.095 \times 53 \times 1000/1000 = 5.035$ g

Thus, Percentage of Sodium Carbonate in Soda Ash = 5.035/5.3 = 95%

A.1.3 Determination of Available CaO % in Quick Lime Powder Sample

Procedure

- 2.804 g pulverized calcium oxide sample was taken in a conical flask containing about 90 ml distilled water
- the flask was kept on heating plate and boiled for 1 minute
- the solution was cooled to room temperature and 100 ml neutralized sugar solution was added into the flask
- the flask was stoppered and swirled for 15 minutes to complete reaction
- removed stopper and the solution was titrated against standard hydrochloric acid in presence of phenolphthalein indicator
- the end point was determined by the first disappearance of pink color

Calculation

Available lime (CaO), % = N ×V×2.804/ W

Where,

N = normality of acid solution

V = volume of HCl consumed, ml

W = weight of sample, g and

2.804 = CaO, g, equivalent to 1 ml of standard acid × 100

Result

Analytical grade calcium oxide was 96%

A.1.4 Determination of Calcium Carbonate Percentage

Procedure

- 4.6 g calcium carbonate sample was weighted and taken in a conical flask
- 100 ml 1.0 N HCl was added and boiled gently for 5 minutes
- the solution was cooled and titrated against 0.5 N NaOH solution using phenolphthalein as indicator

Calculation

% $CaCO_3$(dry) = $5.0045(V_1N_1-V_2N_2)/W$

where,

N_1= normality of acid solution

V_1 = volume of HCl consumed, ml

V_2 = NaOH solution required for titration of excess acid, ml

N_2 = normality of NaOH solution

W = weight of sample, g

Result

98.3-99% for analytical grade reagent.

A.1.5 Determination of $CaCO_3$ % in Calcium Carbonate Powder (at Crescent Chemicals Ltd.)

1.5-2 g of $CaCO_3$ powder sample was taken in 500 ml volumetric flask. It was dissolved with 10% HCl solution (about 20 ml HCl needed). The solution was boiled for 2 minutes and then cooled this solution with flow of water and made volume up to 500 ml.

Procedure

10 ml prepared solution was taken in a conical flask with pipette, then some distilled water and 6 ml 10M NaOH solution were added. Potentiometric titration was done against 0.1M EDTA solution using calcon as indicator. Figure A.1.1 shows the experimental set-up. Result shows in metler: R_1= $CaCO_3$ % and R_2= consumption of EDTA. Before experiment, potential of photo electrode was adjusted at 1000 mV. 1 ml 0.1M EDTA ≡ 10.009 mg $CaCO_3$

Result

98.3% for analytical grade reactants and 96.67% for commercial grade reactants

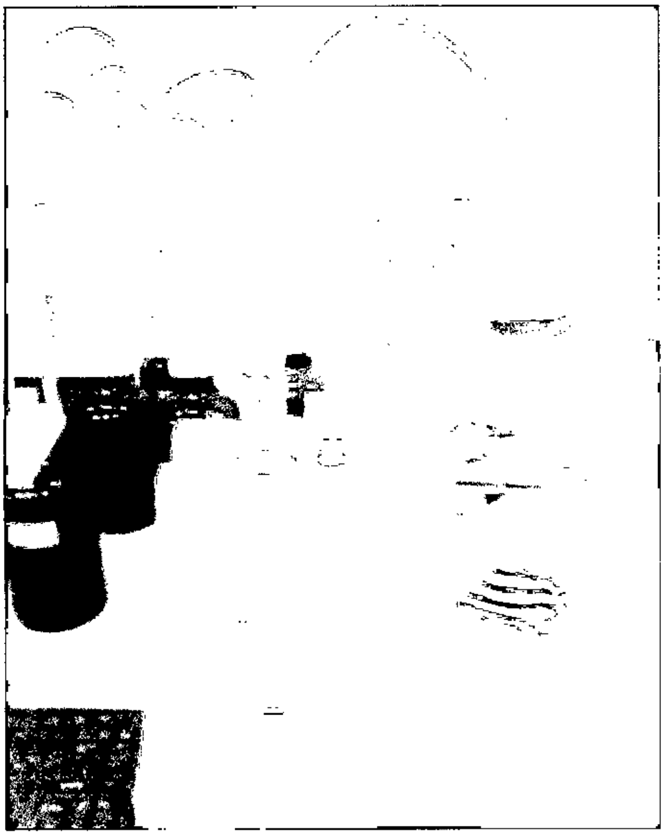

Figure A.1.1: Laboratory instrument for chemical analysis of samples at Crescent Chemicals Ltd.

A.1.6 Chemical Method for Determination of Crystal Structure of $CaCO_3$

Method-1

Procedure

- About 2 g precipitated calcium carbonate was taken in 100 ml water in a measuring cylinder and then 1 g ferrous ammonium sulfate was added with solution.
- The mixture was shaken vigorously for about 4 – 5 minutes. Then the color of the solution was observed

Color of Solution	Structure
Green	Aragonite
Yellow	Calcite
Mixed of both	Both Aragonite & Calcite

Observation

The color changed of solution for both cases were yellow

Result

The precipitated calcium carbonate structure was calcite

Method-2

Procedure

0.2 g Precipitated calcium carbonate (PCC) sample was taken in a conical flask containing about 40-50 ml distilled water. After adding 2 ml 0.1 M HNO_3 acid, the solution was boiled vigorously on heater. When the solution is boiled vigorously then 2 ml 0.1 M cobalt nitrate solution was added.

The solution was kept about 30-40 second on the heater and then the flask was removed from the heater. Cold water was added up to 150 ml and then allowed to cool the conical flask.

Color of Precipitate	Structure
Bluish white	100% Calcite
Deep purple	100% Aragonite

Observation

The color changed of the precipitate was bluish white in both cases

Result

The precipitated calcium carbonate structure was calcite

A.1.7 Scanning Electron Microscope Method for Determination of Crystal Structure of $CaCO_3$ (PCC)

Procedures

- Calcium carbonate powder was converted to tablet at high pressure. Sodium silicate was used as binding agent to give mechanical strength to tablet.
- The tablet was heated at 350^0C for two hours to give thermal strength.
- Gold coating was done at vacuum condition
- The sample finally introduced in the electron microscope chamber and photograph was taken.

Observation

Rhombohedral structure of each sample was observed

Result

The structure of each sample was Calcite

Appendix- A2

Sample Calculation

Appendix- A2 Sample Calculation for Batch 13

Table A.2.1: Observed data for Batch 13

Stage 1 Fresh sodium carbonate: 89.61 g (100% Na_2CO_3) 760 ml recycle washed solution contain 10.28 g NaOH and 1.77 g Na_2CO_3 CaO (96% pure): 45.26 g CaO (90% of stoichiometric ratio)					
Type of Liquid	Total Volume ml	Sample Volume ml	Initial Burette Reading ml	Phenolphthalein End Point ml	Methyl Orange End Point ml
Product	675	10	0	254.2	271
Wash-1	420	10	3.1	45.1	47.9
Wash-2	375	10	23.2	32.5	33.2
Wash-3	455	10	33.4	36	36.2
Stage 2: CaO (96% pure): 9.53 g (50 % excess)					
Product	625	10	1.6	264.7	273.1
Wash-1	360	10	3.2	33.9	35.5
Wash-2	440	10	33.1	39.5	39.9
Wash-3	395	10	42.1	43.8	43.9

<u>Calculation of Strength and Amount</u>

We know,

$$V_1S_1=V_2S_2$$

Here

V_1 = Volume of sample

S_1 = Strength of sodium hydroxide (to be determined)

V_2 = Volume of HCl required to titrate OH^- from a mixture of OH^- and CO_3^{--}

S_2 = Strength of HCl (0.0974 N)

Strength of Sodium Hydroxide:

For Liquid product after stage 1

$$10S_1 = \{(254.2 - 0) - (271 - 254.2)\} \times 0.0974$$

$$S_1 = 2.3123 \text{ N}$$

Amount of Sodium Hydroxide (g) in the Product Liquid:

$$= NeV = 2.3123 \times 40 \times 0.675$$

$$= 62.4315 \text{ g}$$

where,

N = Normality of solution

e = Equivalent weight

V = Volume in liter

Strength of Sodium Carbonate:

For Liquid product after stage 1

$$10S_1 = \{(271 - 254.2) \times 2\} \times 0.0974$$

$$S_1 = 0.3273 \text{ N}$$

Amount of Sodium Carbonate (g) in the Product Liquid:

$$= 0.3273 \times 53 \times 0.675$$

$$= 11.7079 \text{ g}$$

Table A.2.2: Calculated data of strength and amount

Stage 1

Type of Liquid	Total Volume (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	Amount NaOH (g)	Amount Na_2CO_3 (g)
Product	675	2.3123	0.3273	62.4315	11.7079
Wash-1	420	0.3818	0.0545	6.4144	1.2141
Wash-2	375	0.0838	0.0136	1.2565	0.2710
Wash-3	455	0.0234	0.0039	0.4254	0.0940
Total				**70.5277**	**13.2870**
Stage 2					
Product	625	2.4808	0.1636	62.0195	5.4203
Wash-1	360	0.2834	0.0312	4.0814	0.5947
Wash-2	440	0.0584	0.0078	1.0285	0.1817
Wash-3	395	0.0156	0.0019	0.2462	0.0408
Total				**67.3757**	**6.2375**

Table A.2.3: Summary of calculation of percent conversion for Stage 1

Type of liquid	Inlet (g)		Outlet (g)		% conversion	
	NaOH	Na_2CO_3	NaOH	Na_2CO_3	Basis: Na_2CO_3	Basis: CaO
Fresh Feed	×	89.61	×	×	85.7	95.04
Product	×	×	62.4315	11.7079		
Recycle	10.28	1.77	×	×		
Wash-1	0.99	0.18	6.4144	1.2141		
Wash-2	0.27	0.04	1.2565	0.2710		
Wash-3	0.00	0.00	0.4254	0.0940		
Total	**11.54**	**91.6**	**70.5277**	**13.2870**		

Calculation of Percent Conversion

Stage 1

Equivalent amount of NaOH to be produced from feed CaO = 62.07 g

Amount of sodium hydroxide produced = 58.99 g

So, percentage conversion (calcium oxide basis) = 58.99/62.07 = 95.04%

Reacted sodium carbonate = 91.6 -13.29 = 78.31 g

So, percentage conversion = 78.31/91.38 = 85.7%

Total inlet equivalent Na_2CO_3 in Stage 1 = 106.89 g

Total outlet equivalent Na_2CO_3 from Stage 1 = 106.73 g

Unaccounted loss of equivalent Na_2CO_3 = 0.16 g

Recovery of equivalent Na_2CO_3 = 99.86%

Stage 2

Feed:

Sodium hydroxide = 665/675×62.43 = 61.51 g

Sodium carbonate = 665/675×11.71 = 11.54 g

Calcium oxide = 9.53 g

Product Contains:

Sodium hydroxide = 62.02 g

Sodium carbonate = 5.42 g

Inlet First Wash Water Contains:

Sodium hydroxide = 365/375 ×1.26 = 1.23 g

Sodium carbonate = 365/375 ×0.27= 0.26 g

Outlet First Wash Water Contains:

Sodium hydroxide = 4.08 g

Sodium carbonate = 0.60 g

Inlet Second Wash Water Contains:

Sodium hydroxide: 445 / 455× 0.43 = 0.42 g

Sodium carbonate: 445/455 ×0.094 =0.09 g

Outlet Second Wash Water Contains:

Sodium hydroxide = 1.03 g

Sodium carbonate= 0.18 g

Inlet Third Wash Water Contains:

Sodium hydroxide = 0.0 g

Sodium carbonate= 0.0 g

Outlet Third Wash Water Contains:

Sodium hydroxide = 0.25 g

Sodium carbonate= 0.04 g

Table A.2.4: Summary of calculation of percent conversion for Stage 2

Type of liquid	Inlet (g)		Outlet (g)		% conversion	
	NaOH	Na_2CO_3	NaOH	Na_2CO_3	Basis: Na_2CO_3	Basis: CaO
Feed	61.51	11.54	×	×	48.96	33.1
Product	×	×	62.02	5.42		
Wash-1	1.23	0.26	4.08	0.6		
Wash-2	0.42	0.09	1.03	0.18		
Wash-3	0	0	0.25	0.04		
Total	63.16	11.89	67.38	6.24		

Sodium hydroxide produced in the second Stage = 67.38-63.16 = 4.22 g

Sodium carbonate reacted = 11.89 - 6.24 = 5.65 g

% conversion of sodium carbonate = 5.65/11.54 = 48.96 %

% conversion of calcium oxide = 4.22/13.06 = 32.31 %

Total inlet equivalent sodium carbonate in Stage 2 = 95.58 g

Total outlet equivalent sodium carbonate from Stage 2 = 95.52 g

Unaccounted loss of equivalent Na_2CO_3 = 0.06 g

Recovery of equivalent Na_2CO_3 = 99.94%

Overall Conversion

Fresh Sodium carbonate feed to system = 89.61 g

Product sodium hydroxide obtained = 62.02 g

The following block diagram shows **titration losses** in **Batch 12**

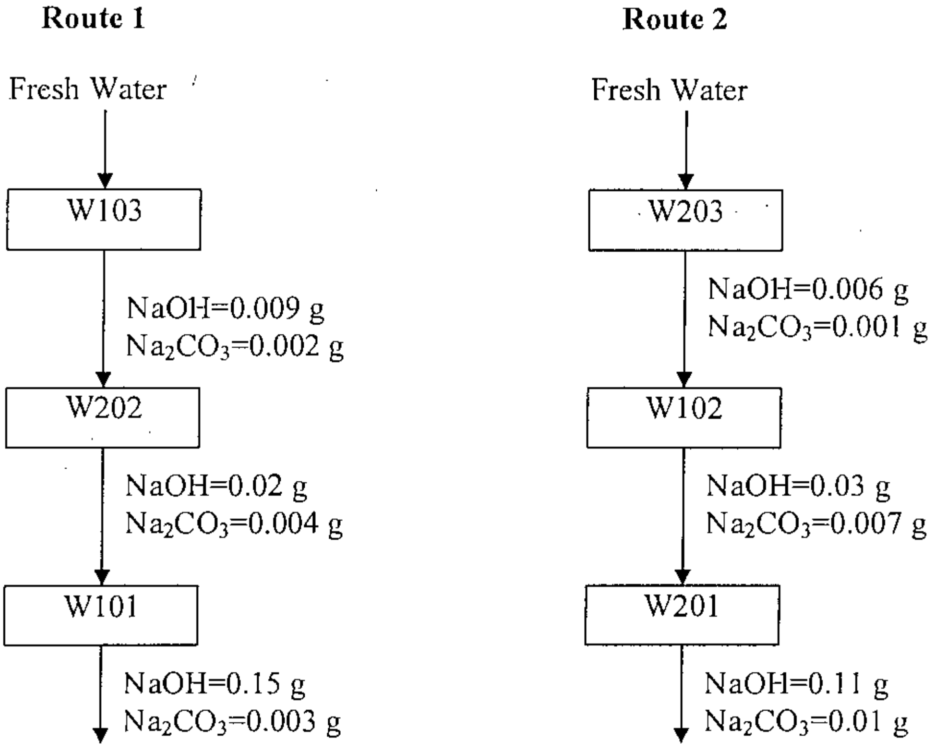

Figure A.2.1: Titration loss in Batch 12

Total NaOH loss from **Batch 12** = 0.33 g, equivalent to 0.44 g Na_2CO_3

Total Na_2CO_3 loss from **Batch 12** = 0.06 g

Total equivalent Na_2CO_3 loss = 0.5 g

So actual fresh Na_2CO_3 feed to system = 89.61 - 0.5 = 89.11 g

Loss of production of NaOH due to titration after Stage 1in batch 13

$= 10/675\times62.43 + (10/675\times11.71) \times 0.49 = 1.01$ g

So actual production after accounting different titration loss = 62.02+1.01 = 63.03 g

Hence actual **overall conversion** for **Batch 13** = (63.03×106) / (89.11× 80) = **93.72%**

Overall recovery = (1-0.22/89.61) × 100 = **99.75%**

Basis: Unreacted Na_2CO_3

Unreacted Na_2CO_3 =5.42 g

Overall conversion = (1-5.42/89.61) = 93.95%

Appendix- A3

Summary of Experimental Data

Appendix- A3 **Summary of Observed and Calculated Data**

A.3.1 Analytical Grade Reactants

Table A.3.1.1: Observed and calculated data for Batch 1

Stage1: Fresh sodium carbonate: 105 g (100% purity)
Water: 735 ml
CaO (96% pure): 40.45 g (70% of stoichiometric amount)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	660	10	0	36.4	43.7	1.8333	0.9198	48.3991	32.1746
Wash-1	220	10	10.4	17.0	18.2	0.3402	0.1512	2.9938	1.7630
Wash-2	200	10	15.1	16.7	17.0	0.0819	0.0378	0.6552	0.4007
Wash-3	240	10	43.1	43.7	43.8	0.0315	0.0126	0.3024	0.1603
Stage 2: CaO (96% pure): 17.05 g (95 % of stoichiometric amount)							**Total**	**52.3505**	**34.4985**
Product	590	10	0.1	43.9	46.3	2.6082	0.3024	61.5535	9.4560
Wash-1	180	10	0.7	7.4	7.7	0.4032	0.0378	2.9030	0.5200
Wash-2	200	10	35.4	36.5	36.6	0.0630	0.0150	0.5040	0.2000
Wash-3	190	10	0	0.45	0.5	0.0252	0.0063	0.1915	0.0634
Stage 3: CaO (96% pure): 7.68 g (50 % excess)							**Total**	**65.1521**	**10.2395**
Product	540	10	2.6	47.3	48.9	2.7153	0.2016	58.6505	5.7698
Wash-1	180	10	36.6	42.3	42.8	0.3276	0.0630	2.3587	0.6010
Wash-2	170	10	0.7	4.1	4.3	0.2016	0.0252	1.3709	0.2271
Wash-3	160	10	6.0	6.65	6.7	0.0378	0.0063	0.2419	0.0534
							Total	**62.6220**	**6.6513**

Table A.3.1.2: Observed and calculated data for Batch 2

Stage1
Fresh sodium carbonate: 85 g (100% pure)
735 ml water
CaO (96% pure): 35.1 g (75% of stoichiometric amount)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	640	10	0.2	31.1	35.9	1.6443	0.6048	42.0941	20.5148
Wash-1	210	10	7.2	14.8	16.1	0.3969	0.1638	3.3340	1.8231
Wash-2	160	10	8.2	10.4	10.7	0.1197	0.0378	0.7661	0.3205
Wash-3	250	10	11.6	12.1	12.2	0.0252	0.0126	0.2520	0.1669
Stage 2: Na_2CO_3: 20 g , CaO (96% pure): 21 g (95 % of stoichiometric amount)							**Total**	**46.4461**	**22.8254**
Product	580	10	2.6	45.65	47.5	2.5956	0.2331	60.2179	7.1655
Wash-1	150	10	33.4	40.6	41	0.6623	0.0779	3.9739	0.6195
Wash-2	220	10	10	11.5	11.6	0.1364	0.0195	1.2000	0.2271
Wash-3	200	10	3.7	4.4	4.5	0.0584	0.0195	0.4675	0.2065
Stage 3: CaO (96% pure): 5.82 g (50 % excess)							**Total**	**65.8593**	**8.2186**
Product	530	10	1.6	30.4	31.4	2.7077	0.1948	57.4037	5.4719
Wash-1	150	10	5.1	10.4	10.7	0.4870	0.0584	2.9220	0.4646
Wash-2	200	10	9.6	10.65	10.8	0.0877	0.0292	0.7013	0.3097
Wash-3	200	10	10.5	10.95	11	0.0390	0.0097	0.3117	0.1032
							Total	**61.3386**	**6.3495**

Table A.3.1.3: Observed and calculated data for Batch 3

Stage 1
Fresh sodium carbonate: 105 g (100% pure)
735 ml water
CaO (96% pure): 44.5 g (80% of stoichiometric amount)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (ml)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	660	10	11.3	35.9	39.6	2.0357	0.7208	53.7414	25.2122
Wash-1	170	10	11.5	17.1	18	0.4578	0.1753	3.1129	1.5796
Wash-2	200	10	33.2	34.4	34.5	0.1071	0.0195	0.8571	0.2065
Wash-3	250	10	34.6	35.1	35.15	0.0438	0.0097	0.4383	0.1291
Stage 2: CaO (96% pure): 12.98 g (95 % of stoichiometric amount)							**Total**	**58.1497**	**27.1274**
Product	590	10	2.7	30.9	32.1	2.6298	0.2338	62.0633	7.3097
Wash-1	180	10	38.2	42.7	43	0.4091	0.0584	2.9454	0.5575
Wash-2	200	10	43.4	44.9	45	0.1364	0.0195	1.0909	0.2065
Wash-3	190	10	45	45.25	45.3	0.0195	0.0097	0.1480	0.0981
Stage 3: CaO (96% pure): 5.7 g (50 % excess)							**Total**	**66.2476**	**8.1718**
Product	535	10	2.7	31.9	32.8	2.7564	0.1753	58.9874	4.9712
Wash-1	185	10	11.2	15.5	15.7	0.3993	0.0390	2.9551	0.3820
Wash-2	175	10	0.2	1.9	2	0.1558	0.0195	1.0909	0.1807
Wash-3	200	10	2.1	2.4	2.44	0.0253	0.0078	0.2026	0.0826
							Total	**63.2360**	**5.6165**

Table A.3.1.4: Observed and calculated data for Batch 4

Stage1
Fresh sodium carbonate: 105 g (100% pure)
735 ml recycle solution (13.45 g NaOH + 6.1 g Na_2CO_3)
CaO (96% pure): 48.91 g (80% of stoichiometric amount)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	650	10	7.7	38.2	41.7	2.6298	0.6818	68.3748	23.4880
Wash-1	260	10	23.2	30.1	30.9	0.5941	0.1558	6.1791	2.1475
Wash-2	250	10	35	36.9	37.2	0.1558	0.0584	1.5584	0.7743
Wash-3	255	10	37.5	37.9	37.94	0.0351	0.0078	0.3577	0.1053
Stage 2: CaO (96% pure): 12.1 g (95 % of stoichiometric amount)							**Total**	**76.4699**	**26.5151**
Product	550	10	7.4	41	43.1	3.0681	0.4091	67.4982	11.9247
Wash-1	270	10	5	11.6	11.8	0.6234	0.0390	6.7323	0.5575
Wash-2	265	10	11.8	13.15	13.2	0.1266	0.0097	1.3422	0.1368
Wash-3	310	10	13.2	13.88	13.9	0.0643	0.0039	0.7971	0.0640
Stage 3: CaO (96% pure): 9.67 g (50 % excess)							**Total**	**76.3698**	**12.6830**
Product	490	10	7.5	43.2	44.2	3.3798	0.1948	66.2437	5.0590
Wash-1	500	10	34.5	36.6	36.7	0.1948	0.0195	3.8960	0.5162
Wash-2	350	10	36.2	36.85	36.9	0.0584	0.0097	0.8182	0.1807
Wash-3	250	10	36.9	37.28	37.3	0.0351	0.0039	0.3506	0.0516
							Total	**71.3085**	**5.8075**

Table A.3.1.5: Observed and calculated data for Batch 5

Stage 1
Fresh sodium carbonate: 105 g (100% pure)
735 ml water
CaO (96% pure): 52 g (90% of stoichiometric amount)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	660	10	2.4	28.2	29.9	2.3473	0.3312	61.9698	11.5840
Wash-1	235	10	31.1	36.9	37.3	0.5260	0.0779	4.9440	0.9705
Wash-2	230	10	37.4	38.9	39.1	0.1266	0.0390	1.1649	0.4749
Wash-3	260	10	38.8	39.3	39.35	0.0438	0.0097	0.4558	0.1342
Stage 2: CaO (96% pure): 9.42 g (50 % excess)							**Total**	**68.5345**	**13.1636**
Product	600	10	1.4	28.5	29.3	2.5616	0.1558	61.4789	4.9557
Wash-1	210	10	12	16.9	17.3	0.4383	0.0779	3.6817	0.8672
Wash-2	240	10	17.8	19	19.1	0.1071	0.0195	1.0285	0.2478
Wash-3	260	10	18.9	19.35	19.4	0.0390	0.0097	0.4052	0.1342
							Total	**66.5943**	**6.2050**

Table A.3.1.6: Observed and calculated data for Batch 6

Stage 1
Equivalent sodium carbonate: 110 g
780 ml recycle stream contain 14 g NaOH and 10.1 g sodium carbonate
CaO (96% pure): 47.3 g (90% of stoichiometric amount)
Fresh sodium carbonate: 81.5 g (100% pure)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	695	10	4.8	30.4	31.9	2.3473	0.2922	65.2561	10.7632
Wash-1	400	10	39.2	42.64	42.9	0.3097	0.0506	4.9557	1.0737
Wash-2	400	10	43	43.7	43.76	0.0623	0.0117	0.9974	0.2478
Wash-3	400	10	31.7	32.16	32.2	0.0409	0.0078	0.6545	0.1652
Stage 2: CaO (96% pure): 8.7 g (50 % excess)							**Total**	**71.8637**	**12.2499**
Product	600	10	3.4	30.60	31.44	2.5675	0.1636	61.6191	5.2035
Wash-1	385	10	32.0	34.90	35.04	0.2688	0.0273	4.1399	0.5565
Wash-2	385	10	32.0	33.16	33.24	0.1052	0.0156	1.6200	0.3180
Wash-3	400	10	34.5	34.98	35.00	0.0448	0.0039	0.7169	0.0826
							Total	**68.0958**	**6.1606**

Table A.4.7: Observed and calculated data for Batch 7

Stage 1
Equivalent sodium carbonate: 105 g
780 ml recycle stream contain 9.73 g NaOH and 5.7 g sodium carbonate
CaO (96% pure): 47.61 g (90% of stoichiometric amount)
Fresh sodium carbonate: 86.4 g (100% pure)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	675	10	0	252.2	269	2.2928	0.3273	61.9055	11.7079
Wash-1	385	10	0	43.35	46.5	0.3915	0.0614	6.0298	1.2521
Wash-2	385	10	4.2	10.85	11.3	0.0604	0.0088	0.9300	0.1789
Wash-3	410	10	11.9	14.3	14.4	0.0224	0.0019	0.3674	0.0423
Stage 2: CaO (96% pure): 9.53 g (50 % excess)							**Total**	**69.2327**	**13.1812**
Product	610	10	0	262.1	270.5	2.4710	0.1636	60.2933	5.2902
Wash-1	370	10	0	32	33.3	0.2990	0.0253	4.4255	0.4966
Wash-2	395	10	0	8.2	8.7	0.0750	0.0097	1.1850	0.2039
Wash-3	395	10	0	4	4.15	0.0375	0.0029	0.5925	0.0612
							Total	**66.4962**	**6.0519**

Table A.3.1.8: Observed and calculated data for Batch 8

Stage 1
Fresh sodium carbonate: 105 g
735 ml water
CaO (96% pure): 52 g + 16 ml water (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	672	10	0	250.7	270	2.2538	0.3760	60.5831	13.3903
Wash-1	420	10	2.1	40.7	43.5	0.3487	0.0545	5.8580	1.2141
Wash-2	375	10	12.2	20.8	21.5	0.0769	0.0136	1.1542	0.2710
Wash-3	457	10	21.2	22.85	23	0.0146	0.0029	0.2671	0.0708
Stage 2: CaO (96% pure): 10.89 g (50 % excess)							**Total**	**67.8624**	**14.9463**
Product	617	10	0	262.3	270.8	2.4720	0.1656	61.0093	5.4146
Wash-1	360	10	1.4	32.6	34.2	0.2883	0.0312	4.1516	0.5947
Wash-2	442	10	8.3	14.5	14.9	0.0565	0.0078	0.9988	0.1825
Wash-3	395	10	0.1	2.1	2.2	0.0185	0.0019	0.2924	0.0408
							Total	**66.452**	**6.2326**

Table A.3.1.9: Observed and calculated data for Batch 9

Stage1
Equivalent sodium carbonate: 105 g
760 ml Volume of dilute caustic solution contain 9.76 g NaOH and 1.76 g sodium carbonate
CaO (96% pure): 45.6 g (90% of stoichiometric ratio)
Fresh feed sodium carbonate: 90.31g

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthale in End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	675	10	0	253.1	270	2.3006	0.3292	62.1159	11.7776
Wash-1	420	10	2.1	43.5	46.2	0.3769	0.0526	6.3326	1.1708
Wash-2	380	10	0	9.6	10.35	0.0862	0.0146	1.3102	0.2942
Wash-3	450	10	10.5	13.9	14.1	0.0312	0.0039	0.5610	0.0925
Stage 2: CaO (96% pure): 9.58 g (50 % excess)							**Total**	**70.3197**	**13.3351**
Product	625	10	0.2	262.7	271.1	2.4749	0.1636	61.8734	5.4203
Wash-1	360	10	0.7	31.5	33	0.2795	0.0292	4.1095	0.5575
Wash-2	438	10	2.5	8.7	9.1	0.0565	0.0078	0.9897	0.1809
Wash-3	395	10	12.1	14.3	14.4	0.0205	0.0019	0.3232	0.0408
							Total	**67.2958**	**6.1995**

Table A.3.1.10: Observed and calculated data for Batch 10

Stage 1
Equivalent sodium carbonate: 105 g
Fresh sodium carbonate: 89.72 g
760 ml recycle washed solution contain 10.26 g NaOH and 1.69 g Na_2CO_3
CaO (96% pure): 45.27 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	670	10	0	255.7	272.6	2.3259	0.3292	62.3344	11.6903
Wash-1	420	10	0.8	42.9	45.8	0.3818	0.0565	6.4144	1.2575
Wash-2	375	10	22.8	32.5	33.2	0.0877	0.0136	1.3149	0.2710
Wash-3	455	10	33.1	36	36.2	0.0263	0.0039	0.4786	0.0940
Stage 2: CaO (96% pure): 9.51 g (50 % excess)							**Total**	**70.5423**	**13.3128**
Product	620	10	0	264.2	272.7	2.4905	0.1656	61.8373	5.4410
Wash-1	370	10	2.0	32.7	34.2	0.2844	0.0292	4.0955	0.5575
Wash-2	440	10	33.2	39.5	39.9	0.0575	0.0078	1.0114	0.1817
Wash-3	395	10	41.4	43.8	43.9	0.0224	0.0019	0.3540	0.0408
							Total	**67.2981**	**6.2210**

Table A.3.1.11: Observed and calculated data for Batch 11

Stage 1
Equivalent sodium carbonate: 105 g
Fresh sodium carbonate: 89.74 g
760 ml recycle washed solution contain 10.25 g NaOH and 1.68 g Na_2CO_3
CaO (96% pure): 45.28 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	670	10	0.3	256.3	273.2	2.3288	0.3292	62.4128	11.6903
Wash-1	420	10	0.1	42.3	45.2	0.382	0.0565	6.4307	1.2575
Wash-2	390	10	21.5	30.5	31.2	0.0808	0.0136	1.2611	0.2819
Wash-3	457	10	34.3	37.2	37.4	0.0263	0.0039	0.4807	0.0944
Stage 2: CaO (96% pure): 9.51 g (50 % excess)							**Total**	**70.5854**	**13.3241**
Product	625	10	1.9	264.8	273.2	2.4788	0.1636	61.9708	5.4203
Wash-1	360	10	0.1	30.6	32.1	0.2825	0.0292	4.0674	0.5575
Wash-2	440	10	10.8	17	17.4	0.0565	0.0078	0.9943	0.1817
Wash-3	405	10	17.4	19.5	19.6	0.0195	0.0019	0.3156	0.0418
							Total	**67.3480**	**6.2014**

Table A.3.1.12: Observed and calculated data for Batch 12

Stage 1
Equivalent sodium carbonate: 105 g
Fresh sodium carbonate: 89.65 g
760 ml recycle washed solution contain 10.22 g NaOH and 1.81g Na_2CO_3
CaO (96% pure): 45.3 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	672	10	0	255.4	272.3	2.3230	0.3292	62.4420	11.7252
Wash-1	420	10	2.9	45.1	48	0.3828	0.0565	6.4307	1.2575
Wash-2	375	10	23.1	32.5	33.2	0.0847	0.0136	1.2711	0.2710
Wash-3	455	10	33.5	36	36.2	0.0224	0.0039	0.4077	0.0940
Stage 2:	CaO (96% pure): 9.54 g (50 % excess)						**Total**	**70.5515**	**13.3477**
Product	620	10	0	265.1	273.6	2.4993	0.1656	61.9822	5.4410
Wash-1	360	10	3.1	33.9	35.4	0.2854	0.0292	4.1095	0.5575
Wash-2	440	10	33.2	39.5	39.9	0.0575	0.0078	1.0114	0.1817
Wash-3	395	10	41.9	43.8	43.9	0.0175	0.0019	0.2770	0.0408
							Total	**67.3802**	**6.2210**

A.3.2 Commercial Grade Reactants

Table A.3.2.1: Observed and calculated data for Batch 1

Stage 1
Fresh sodium carbonate: 110.5 g (95% pure)
Water: 735 ml
$Ca(OH)_2$ (93% pure): 70.94 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	640	10	1	252.6	268.6	2.2947	0.3117	58.7454	10.5722
Wash-1	420	10	3.7	59.8	64.2	0.5036	0.0857	8.4598	1.9079
Wash-2	375	10	8.6	21.1	22.2	0.1110	0.0214	1.6655	0.4259
Wash-3	455	10	22.1	24.2	24.4	0.0185	0.0039	0.3368	0.0940
Stage 2: $Ca(OH)_2$ (93% pure): 11.82 g (50 % excess)							**Total**	**69.2076**	**13.0000**
Product	600	10	10.7	262.2	270.4	2.3697	0.1597	56.8738	5.0796
Wash-1	360	10	0.1	37.2	39.3	0.3409	0.0409	4.9090	0.7805
Wash-2	435	10	15.8	24	24.4	0.0760	0.0078	1.3219	0.1796
Wash-3	395	10	24.3	26.4	26.5	0.0195	0.0019	0.3078	0.0408
							Total	**63.4125**	**6.0806**

Table A.3.2.2: Observed and calculated data for Batch 2

Stage 1
Equivalent sodium carbonate: 105 g
Fresh Sodium Carbonate: 89.52 g (95% pure)
760 ml recycle feed contains = 13.03 g NaOH + 2.69 g Na_2CO_3which is equivalent to 19.96 g Na_2CO_3
$Ca(OH)_2$ (93% pure): 59.27 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	640	10	0.3	254.7	268.2	2.3464	0.2630	60.0670	8.9203
Wash-1	420	10	11.3	75.5	78.9	0.5922	0.0662	9.9488	1.4743
Wash-2	375	10	14.9	30	31	0.1373	0.0195	2.0600	0.3872
Wash-3	455	10	4.7	7.8	8	0.0282	0.0039	0.5141	0.0940
Stage 2: $Ca(OH)_2$ (93% pure): 9.2 g (50 % excess)							**Total**	**72.5899**	**10.8757**
Product	600	10	6.7	263	271.1	2.4175	0.1578	57.5357	4.9758
Wash-1	360	10	12.1	49.3	51.1	0.3448	0.0351	4.9651	0.6690
Wash-2	435	10	4.5	12.5	13	0.0731	0.0097	1.2711	0.2246
Wash-3	395	10	0.3	2.3	2.4	0.0185	0.0019	0.2924	0.0408
							Total	**64.0643**	**5.9102**

Table A.3.2.3: Observed and calculated data for Batch 3

Stage 1
Equivalent sodium carbonate: 105 g
Fresh sodium carbonate: 88.05 g (95% pure)
760 ml recycle feed contains = 14.56 g NaOH + 2.09 g Na_2CO_3which is equivalent to 21.35 g Na_2CO_3
$Ca(OH)_2$ (93% pure): 57.92 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	645	10	1.5	253.1	265.9	2.3259	0.2493	60.0085	8.5238
Wash-1	420	10	0.1	66.1	69.3	0.6117	0.0623	10.2761	1.3876
Wash-2	375	10	18.1	33.9	35.1	0.1422	0.0234	2.1331	0.4646
Wash-3	455	10	37.1	40	40.2	0.0263	0.0039	0.4786	0.0940
Stage 2: $Ca(OH)_2$ (93% pure): 9.45 g (50 % excess)							**Total**	**72.8963**	**10.4700**
Product	600	10	1.3	254.1	262.2	2.3834	0.1578	57.2011	5.0177
Wash-1	360	10	7.5	45	46.9	0.3467	0.0370	4.9931	0.7062
Wash-2	435	10	33.7	41.5	41.9	0.0721	0.0078	1.2541	0.1796
Wash-3	395	10	42.6	45	45.1	0.0224	0.0019	0.3540	0.0408
							Total	**63.8023**	**5.9443**

Table A.3.2.4: Observed and calculated data for Batch 4

Stage 1
Equivalent sodium carbonate: 105 g
Fresh sodium carbonate: 87.63 g (95% pure)
760 ml recycle feed contains = 14.89 g NaOH + 2.03 g Na_2CO_3 which is equivalent to 21.75 g Na_2CO_3
$Ca(OH)_2$ (93% pure): 57.61 g (90% of stoichiometric ratio)

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	635	10	0.2	255.9	269.1	2.3620	0.2571	59.9935	8.6539
Wash-1	420	10	0.5	66.4	69.3	0.6136	0.0565	10.3088	1.2575
Wash-2	375	10	21.3	36.8	37.8	0.1412	0.0195	2.1185	0.3872
Wash-3	455	10	37.2	40	40.2	0.0253	0.0039	0.4609	0.0940
Stage 2: $Ca(OH)_2$ (93% pure): 9.59 g (50 % excess)							**Total**	**72.8817**	**10.3925**
Product	595	10	7.9	262.7	270.9	2.4019	0.1597	57.1648	5.0373
Wash-1	360	10	3.4	41.1	43.1	0.3477	0.0390	5.0071	0.7434
Wash-2	435	10	7.9	15.7	16.2	0.0711	0.0097	1.2372	0.2246
Wash-3	395	10	15.2	17.2	17.3	0.0185	0.0019	0.2924	0.0408
							Total	**63.7015**	**6.0460**

Table A.3.2.5: Observed and calculated data for Batch 5

Stage 1
Fresh sodium carbonate: 87.68 g (95% pure)
760 ml recycle feed contains = 14.93 g NaOH + 1.94 g Na_2CO_3which is equivalent to 21.7 g Na_2CO_3
$Ca(OH)_2$ (93% pure): 57.58 g (90% of stoichiometric ratio)
Equivalent sodium carbonate: 105 g

Type of Liquid	Total Volume (ml)	Sample Volume (ml)	Initial Burette Reading (ml)	Phenolphthalein End Point (ml)	Methyl Orange End Point (ml)	Strength. of NaOH (N)	Strength. of Na_2CO_3 (N)	NaOH (g)	Na_2CO_3 (g)
Product	640	10	1.6	255.6	268.7	2.3464	0.2552	60.0670	8.6560
Wash-1	420	10	0.8	66.4	69.4	0.6097	0.0584	10.2434	1.3009
Wash-2	375	10	31.4	46.8	47.9	0.1393	0.0214	2.0892	0.4259
Wash-3	455	10	0.2	3.1	3.2	0.0273	0.0019	0.4964	0.0470
Stage 2: $Ca(OH)_2$ (93% pure): 9.59 g (50 % excess)							**Total**	**72.8959**	**10.4297**
Product	600	10	6.9	259.7	267.9	2.3824	0.1597	57.1777	5.0796
Wash-1	360	10	13.5	51.2	53.1	0.3487	0.0370	5.0212	0.7062
Wash-2	435	10	9.5	17.3	17.9	0.0701	0.0117	1.2202	0.2695
Wash-3	395	10	15.2	17.2	17.3	0.0185	0.0019	0.2924	0.0408
							Total	**63.7115**	**6.0960**

Appendix- B

Material Safety Data Sheet for Sodium Hydroxide

Appendix- B Material Safety Data Sheet for Sodium Hydroxide[20]

Sodium hydroxide: solid, pellets or beads

ACC# 21300

Section 1 - Chemical Product and Company Identification

MSDS Name: Sodium hydroxide, solid, pellets or beads

Synonyms: Caustic soda; Soda lye; Sodium hydrate; Lye.

Section 2 - Composition, Information on Ingredients

Table B.I: Composition of caustic soda

CAS#	Chemical Name	Percent	EINECS/ELINCS
497-19-8	Sodium carbonate	<3	207-838-8
1310-73-2	Sodium hydroxide	95-100	215-185-5

Hazard Symbols: C
Risk Phrases: 35

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

Appearance: White. **Danger!** Corrosive. Causes eye and skin burns. Hygroscopic. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns.

Target Organs: Eyes, skin, mucous membranes.

Potential Health Effects

Eye: Causes eye burns. May cause chemical conjunctivitis and corneal damage.

Skin: Causes skin burns. May cause deep, penetrating ulcers of the skin. May cause skin rash (in milder cases), and cold and clammy skin with cyanosis or pale color.

Ingestion: May cause severe and permanent damage to the digestive tract. Causes gastrointestinal tract burns. May cause perforation of the digestive tract. Causes severe pain, nausea, vomiting, diarrhea, and shock. May cause corrosion and permanent tissue destruction of the esophagus and digestive tract. May cause systemic effects.

Inhalation: Irritation may lead to chemical pneumonitis and pulmonary edema. Causes severe irritation of upper respiratory tract with coughing, burns, breathing difficulty, and possible coma. Causes chemical burns to the respiratory tract.

Chronic: Prolonged or repeated skin contact may cause dermatitis. Effects may be delayed.

Section 4 - First Aid Measures

Eyes: In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical aid immediately.

Skin: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid immediately. Wash clothing before reuse.

Ingestion: If swallowed, do NOT induce vomiting. Get medical aid immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.

Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid.

Notes to Physician: Treat symptomatically and supportively.

Section 5 - Fire Fighting Measures

General Information: As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. Use water spray to keep fire-exposed containers cool. Use water with caution and in flooding amounts. Contact with moisture or water may generate sufficient heat to ignite nearby combustible materials. Contact with metals may evolve flammable hydrogen gas.

Extinguishing Media: Substance is noncombustible; use agent most appropriate to extinguish surrounding fire. Do NOT get water inside containers.

Section 6 - Accidental Release Measures

General Information: Proper personal protective equipment should be used as indicated in Section 8.

Spills/Leaks: Vacuum or sweep up material and place into a suitable disposal container. Avoid runoff into storm sewers and ditches which lead to waterways. Clean up spills immediately, observing precautions in the Protective Equipment section. Avoid generating dusty conditions. Provide ventilation. Do not get water on spilled substances or inside containers.

Section 7 - Haudling and Storage

Handling: Wash thoroughly after handling. Do not allow water to get into the container because of violent reaction. Minimize dust generation and accumulation. Do not get in eyes, on skin, or on clothing. Keep container tightly closed. Avoid ingestion and inhalation. Discard contaminated shoes. Use only with adequate ventilation.

Storage: Store in a tightly closed container. Store in a cool, dry, well-ventilated area away from incompatible substances. Keep away from metals. Corrosives area. Keep away from acids. Store protected from moisture. Containers must be tightly closed to prevent the conversion of NaOH to sodium carbonate by the CO_2 in air.

Section 8 - Exposure Controls, Personal Protection

Engineering Controls: Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.

Exposure Limits

Table B.2: Exposure limits of caustic soda

Chemical Name	ACGIH	NIOSH	OSHA - Final PELs
Sodium carbonate	none listed	none listed	none listed
Sodium hydroxide	C 2 mg/m^3	10 mg/m^3 IDLH	2 mg/m^3 TWA

OSHA Vacated PELs: Sodium carbonate: No OSHA Vacated PELs are listed for this chemical. Sodium hydroxide: C 2 mg/m^3

Personal Protective Equipment

Eyes: Wear chemical goggles.

Skin: Wear appropriate protective gloves to prevent skin exposure.

Clothing: Wear appropriate protective clothing to prevent skin exposure.

Respirators: A respiratory protection program that meets OSHA's 29 CFR ?1910.134 and ANSI Z88.2 requirements or European Standard EN 149 must be followed whenever workplace conditions warrant a respirator's use.

Section 9 - Physical and Chemical Properties

Physical State: Solid
Appearance: White
Odor: Odorless
pH: 14 (5% aqueous solution)
Vapor Pressure: 1 mm Hg @739 deg C
Vapor Density: Not available.
Evaporation Rate: Not available.
Viscosity: Not available.
Boiling Point: 1390 deg C @ 760 mm Hg
Freezing/Melting Point: 318 deg C

Auto ignition Temperature: Not applicable.
Flash Point: Not applicable.
Decomposition Temperature: Not available.
NFPA Rating: (estimated) Health: 3; Flammability: 0; Reactivity: 1
Explosion Limits, Lower: Not available.
Upper: Not available.
Solubility: Soluble.
Specific Gravity/Density: 2.13 g/cm^3
Molecular Formula: NaOH
Molecular Weight: 40.00

Section 10 - Stability and Reactivity

Chemical Stability: Stable at room temperature in closed containers under normal storage and handling conditions.

Conditions to Avoid: Moisture, contact with water, exposure to moist air or water, prolonged exposure to air.

Incompatibilities with Other Materials: Acids, water, flammable liquids, organic halogens, metals, aluminum, zinc, tin, leather, wool, nitromethane.

Hazardous Decomposition Products: Toxic fumes of sodium oxide.

Hazardous Polymerization: Will not occur.

Section 11 - Toxicological Information

RTECS#:
CAS# 497-19-8: VZ4050000
CAS# 1310-73-2: WB4900000

LD50/LC50:

CAS# 497-19-8:

Draize test, rabbit, eye: 100 mg/24Hr Moderate;

Draize test, rabbit, eye: 50 mg Severe;

Draize test, rabbit, skin: 500 mg/24Hr Mild;

Inhalation, mouse: LC50 = 1200 mg/m^3/2Hr;

Inhalation, rat: LC50 = 2300 mg/m^3/2Hr;

Oral, mouse: LD50 = 6600 mg/kg;

Oral, rat: LD50 = 4090 mg/kg;<BR.

CAS# 1310-73-2:

Draize test, rabbit, eye: 400 µg Mild;

Draize test, rabbit, eye: 1% Severe;

Draize test, rabbit, eye: 50 µg/24Hr Severe;

Draize test, rabbit, eye: 1 mg/24Hr Severe;

Draize test, rabbit, skin: 500 mg/24Hr Severe;<BR.

Carcinogenicity:

CAS# 497-19-8: Not listed by ACGIH, IARC, NIOSH, NTP, or OSHA.

CAS# 1310-73-2: Not listed by ACGIH, IARC, NIOSH, NTP, or OSHA.

Epidemiology: No information available.

Teratogenicity: No information available.

Reproductive Effects: No information available.

Neurotoxicity: No information available.

Mutagenicity: No information available.

Other Studies: See actual entry in RTECS for complete information.

Section 12 - Ecological Information

No information is available.

Section 13 - Disposal Considerations

Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. US EPA guidelines for the classification determination are listed in 40

CFR Parts 261.3. Additionally, waste generators must consult state and local hazardous waste regulations to ensure complete and accurate classification.

RCRA P-Series: None listed.

RCRA U-Series: None listed.

Section 14 - Transport Information

Table B.3: Transport information

	US DOT	IATA	RID/ADR	IMO	Canada TDG
Shipping Name:	SODIUM HYDROXIDE, SOLID				SODIUM HYDROXIDE
Hazard Class:	8				8(9.2)
UN Number:	UN1823				UN1823
Packing Group:	II				II

Section 15 - Regulatory Information

US FEDERAL

TSCA

CAS# 497-19-8 is listed on the TSCA inventory.

CAS# 1310-73-2 is listed on the TSCA inventory.

Health & Safety Reporting List

None of the chemicals are on the Health & Safety Reporting List.

Chemical Test Rules

None of the chemicals in this product are under a Chemical Test Rule.

Section 12b

None of the chemicals are listed under TSCA Section 12b.

TSCA Significant New Use Rule

None of the chemicals in this material have a SNUR under TSCA.

SARA

Section 302 (RQ)

CAS# 1310-73-2: final RQ = 1000 pounds (454 kg)

Section 302 (TPQ)

None of the chemicals in this product have a TPQ.

SARA Codes

CAS # 497-19-8: acute. CAS # 1310-73-2: acute, reactive.

Section 313

No chemicals are reportable under Section 313.

Clean Air Act

This material does not contain any hazardous air pollutants. This material does not contain any Class 1 Ozone depletors. This material does not contain any Class 2 Ozone depletors.

Clean Water Act

CAS# 1310-73-2 is listed as a Hazardous Substance under the CWA. None of the chemicals in this product are listed as Priority Pollutants under the CWA. None of the chemicals in this product are listed as Toxic Pollutants under the CWA

OSHA

None of the chemicals in this product are considered highly hazardous by OSHA

STATE

CAS# 497-19-8 is not present on state lists from CA, PA, MN, MA, FL, or NJ.

CAS# 1310-73-2 can be found on the following state right to know lists: California, New Jersey, Florida, Pennsylvania, Minnesota, and Massachusetts.

California No Significant Risk Level: None of the chemicals in this product are listed.

European/International Regulations

European Labeling in Accordance with EC Directives

Hazard Symbols: C

Risk Phrases:

R 35: Causes severe burns.

Safety Phrases

S 26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S 37/39: Wear suitable gloves and eye/face protection.

S 45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

WGK (Water Danger/Protection)

CAS# 497-19-8: 1

CAS# 1310-73-2: 1

Canada

CAS# 497-19-8 is listed on Canada's DSL List. CAS# 497-19-8 is listed on Canada's DSL List. CAS# 1310-73-2 is listed on Canada's DSL List. CAS# 1310-73-2 is listed on Canada's DSL List.

This product has a WHMIS classification of E.

CAS# 497-19-8 is listed on Canada's Ingredient Disclosure List.

CAS# 1310-73-2 is listed on Canada's Ingredient Disclosure List.

Exposure Limits

CAS# 1310-73-2:

OEL-AUSTRALIA: TWA 2 mg/m^3

OEL-BELGIUM: STEL 2 mg/m^3
OEL-DENMARK: TWA 2 mg/m^3
OEL-FINLAND: TWA 2 mg/m^3
OEL-FRANCE: TWA 2 mg /m^3
OEL-GERMANY: TWA 2 mg/m^3
OEL-JAPAN: STEL 2 mg/m^3
OEL-THE NETHERLANDS: TWA 2 mg/m^3
OEL-THE PHILIPPINES: TWA 2 mg/m^3
OEL-SWEDEN: TWA 2 mg/m^3
OEL-SWITZERLAND: TWA 2 mg/m^3; STEL 4 mg/m^3
OEL-THAILAND:TWA 2 mg/m^3
OEL-TURKEY:TWA 2 mg/m^3
OEL-UNITED KINGDOM:TWA 2 mg/m^3;STEL 2 mg/m^3
OEL IN BULGARIA, COLOMBIA, JORDAN, KOREA check ACGIH TLV, OEL IN NEW ZEALAND, SINGAPORE, VIETNAM check ACGI TLV

Section 16 - Additional Information

Users should make their own investigations to determine the suitability of the information for their particular purposes. In no event shall Fisher be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if Fisher has been advised of the possibility of such damages.

Appendix-C

Reactants and its Properties

Appendix-C Reactants and its Properties

C.1 Calcium Oxide

Calcium oxide (CaO), commonly known as burnt lime, caustic lime, lime or quicklime, is a widely used chemical compound. It is a white, caustic and alkaline crystalline solid. As a commercial product lime often also contains magnesium oxide, silicon oxide and smaller amounts of aluminium oxide and iron oxide[23].

Calcium oxide is usually made by the thermal decomposition of materials such as limestone, that contain calcium carbonate ($CaCO_3$; mineral name: calcite) in a lime kiln. This is accomplished by heating the material to above 825°C, a process called calcination or lime-burning, to liberate a molecule of carbon dioxide (CO_2); leaving CaO. This process is reversible, since once the quicklime product has cooled, it immediately begins to absorb carbon dioxide from the air, until, after enough time, it is completely converted back to calcium carbonate. Calcination of limestone is one of the first chemical reactions discovered by man and was known in prehistory. The annual lime production is around 130 million tonnes, with the USA and China the largest producers, each producing around 20 million tonnes[23].

C.2 Calcium Hydroxide

Calcium hydroxide, also known as slaked lime, is a chemical compound with the chemical formula $Ca(OH)_2$. It is a colorless crystal or white powder, and is obtained when calcium oxide (called lime or quicklime) is slaked with water. It can also be precipitated by mixing an aqueous solution of calcium chloride and an aqueous solution of sodium hydroxide. A traditional name for calcium hydroxide is slaked lime, or hydrated lime. The name of the natural mineral is portlandite[24].

CaO produces heat energy by the formation of $Ca(OH)_2$, as in the following equation:

$$CaO + H_2O \leftrightarrow Ca(OH)_2 + 15.17 \text{ Kcal/g-mol of CaO}$$

If heated to 512°C, calcium hydroxide decomposes into calcium oxide and water. A suspension of fine calcium hydroxide particles in water is called milk of lime. The solution is called lime water and is a medium strength base that reacts violently with acids and attacks many metals in presence of water. It turns milky if carbon dioxide is passed through, due to precipitation of calcium carbonate[24]. Some physical properties of calcium hydroxide are shown in Table C.1. Figure C.1 shows variation of solubility of CaO and $Ca(OH)_2$ in water with temperature.

Table C.1: Physical properties of calcium hydroxide

Molar mass	74.093 g/mol
Appearance	Soft white powder/Colorless liquid
Crystal Structure	hexagonal
Density and phase	2.211 g/cm³, solid
Solubility in water	0.185 g/100 cm³, $K_{sp} = 7.9 \times 10^{-6}$
Melting point	512°C (decomposes).
Boiling point	N/A
Basicity (pK_b)	-2.37
Specific Heat Capacity	1.18095 J/g-°C
Heat of formation	-985.2 kJ/mol

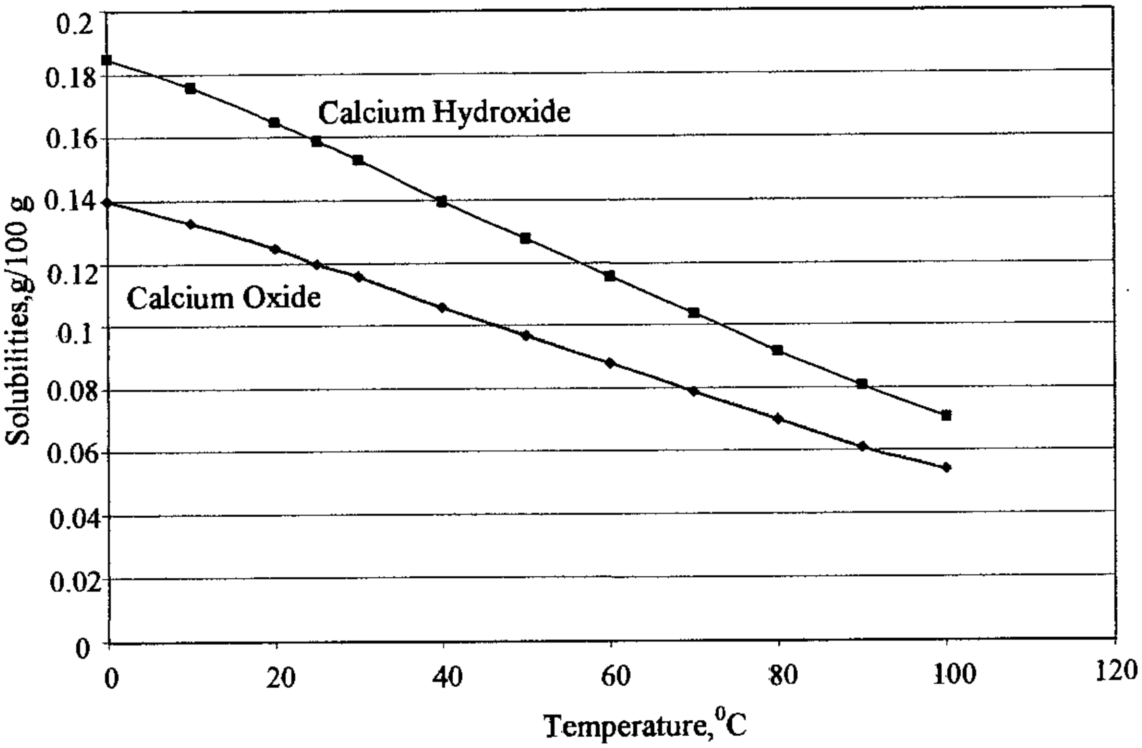

Figure C.1: Variation of solubility of calcium hydroxide and calcium oxide in water with temperature[32]

C.2.1 Uses

Because of its strong basic properties, calcium hydroxide has varied uses, such as

- A flocculant, in water and sewage treatment and improvement of acid soils
- An ingredient in whitewash, mortar, and plaster
- An alkali used as a lye substitute in no-lye hair relaxers
- A chemical depilatory agent found in Nair
- A chemical reagent
    - In the reef aquarium hobby for adding bio-available calcium in solution for calcium-using animals such as algae, snails, hard tube worms, and Corals (often referred to as Kalkwasser mix)
    - In the tanning industry for neutralization of extra acid
    - In the petroleum refining industry for the manufacture of additives to oils (salicatic, sulphatic, fenatic)
    - In the chemical industry for manufacture of calcium stearate
    - In the food industry for processing water (for alcoholic and soft drinks)
    - For clearing a brine of carbonates of calcium and magnesium in the manufacture of salt for food and pharmacopoeia
    - In Native American and Latin American cooking, calcium hydroxide is called "cal". Corn cooked with cal becomes nixtamal which significantly increases its nutrition value, and is also considered tastier and easier to digest.
    - In chewing Betel nut or coca leaves, calcium hydroxide is usually chewed alongside to keep the alkaloid stimulants chemically available for absorption by the body
- A filler
    - In the petrochemical industry for manufacturing solid oil of various marks
    - In the manufacture of brake pads
    - In the manufacture of ebonite
    - For preparation of dry mixes for painting and decorating
    - In manufacturing mixes for pesticides
    - In manufacturing a drug called "Polikar" for fighting decay (due to fungus) of fruits and vegetables during storage

- A dressing in paste form used for anti-microbial effect during a dental root canal procedure.

C.3 Soda Ash

C.3.1 Physical Properties

Specific Gravity:	2.53
Solubility in water (22°C):	22 g/100 ml
Melting Point:	851.0°C
Boiling Point:	Decomposes before melting
p^H (1% aq. soln.):	11.5

- Sodium carbonate is an odourless, opaque white, crystalline or granular solid.
- It is soluble in water and insoluble in alcohol, acetone, and ether. Sodium carbonate reacts exothermically with strong acids evolving carbon dioxide.
- It corrodes aluminium, lead and iron.

C.3.2 Markets and Applications

Soda Ash, known chemically as sodium carbonate (Na_2CO_3), has been used since the earliest recorded times. More than 5000 years ago, the Egyptians made glass ornaments from sodium carbonate recovered from dried desert-basin lakes[31].

Over the years the production techniques have evolved from the method employed by the Egyptians to the Solvay process (also known as the ammonia-soda process) and finally to the most efficient and environmentally friendly process - the refining of soda ash from rich, pure trona deposits located in Wyoming, U.S.A.[31].

As the production capabilities have changed and evolved, so have the various markets and applications for soda ash. Today soda ash consistently ranks as one of the top 10 inorganic chemicals produced in the U.S. and is an essential raw material to a variety of industries. Figure C.3 shows the Consumption of Soda Ash in the United States, by market, in 2005. This data is compiled by the U.S. Geological Survey, a bureau of the U.S. Department of the Interior[31].

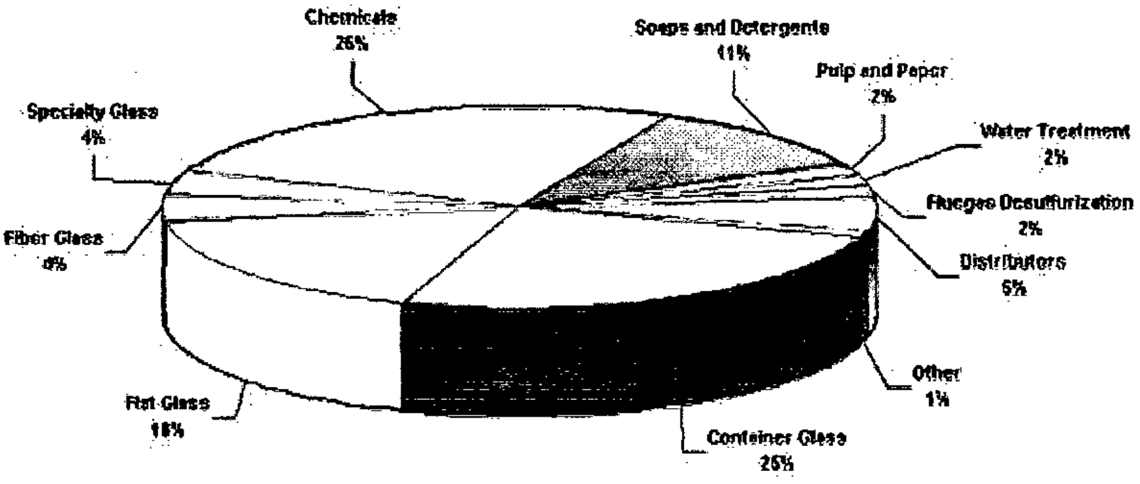

Figure C.3: Consumption of soda ash in U.S.A.[31]

Applications of Soda Ash

Glass Production

The largest single use of soda ash throughout history has been the production of glass. Soda ash commonly contributes about 12% - 15% of the weight of raw materials making up glass. Soda ash, with its low melting point and reactivity, acts as a flux for other ingredients, primarily silica and other oxides, allowing them to be melted at reasonable temperatures and to have a low enough viscosity to be easily handled and formed[31].

Soap and Detergents

Approximately 11% of the soda ash consumed in the US is used in the production of detergents, soaps and cleaning compounds. Soda Ash is used primarily as a builder or filler in formulations of soaps, detergents and other cleaning compounds. In addition to these roles soda ash may also add benefit as an agglomerating aid, a carrier for surfactants and as a source of alkalinity for p^H adjustment[31].

Water Treatment

Soda Ash is a base and therefore finds application in the water treatment segment by adjusting the p^H of water when it is in acidic condition. Because soda ash is safer to handle than other alkalis and its pricing is more stable over time, more and more companies are choosing soda ash to assist in their water treatment needs[31].

Pulp and Paper

Soda Ash has a variety of uses in this market segment ranging from pulp digestion to water treatment. The primary opportunity for soda ash in the segment is in the replacement of caustic soda, which has historically demonstrated more dramatic price fluctuations[31].

Flue Gas Desulfurization

Driven by the US Environmental Protection Agency's requirements governing removal of Sulfur Dioxide (SO_2) from utility stack (flue) gas even when burning low sulfur coal, soda ash has found application in this market segment either as a dry sorbent or as a feedstock in the conversion to sodium bicarbonate[31].

Chemicals

Approximately 26% of the soda ash consumed in the US market is from the production of other chemicals. Soda ash is the least expensive soluble alkali and finds numerous applications in the production of other chemicals such as[31]:

- Chromium Chemicals
- Phosphorous Chemicals
- Sodium Silicates
- Sodium Bicarbonate
- Sodium Hydroxide
- Sodium Sulfite
- Sodium Metabisulfite

Appendix-D

Assay Composition of Reactants

Appendix-D Assay Composition of Reactants

Table D.1: Assay of analytical grade soda ash

Component	Percent
Na_2CO_3	≤99.5-100.5%
Chloride (Cl^-)	≤0.0125
Sulfate ($SO_4^=$)	≤0.025
Arsenic (As)	≤0.001
Lead (Pb)	≤0.0005
Iron (Fe)	≤0.005

Table D.2: Assay of analytical grade calcium oxide

Component	Percent
CaO	≥97
Chloride (Cl^-)	≤0.05
Sulfate ($SO_4^=$)	≤0.5
Insoluble in HCl	≤0.1
Lead (Pb)	≤0.005
Iron (Fe)	≤0.05

Table D.3: Assay of commercial grade soda ash

Component	Percent
Na_2CO_3	≤95
Moisture	4

Table D.4: Assay of commercial grade slaked lime

Component	Percent
$Ca(OH)_2$	93
$CaCO_3$	3
Moisture	1
SiO_2	0.4
Mg	0.59
Fe	0.01
CO_2	1.5
Dead burnt lime	0.5

Appendix -E

Crystal Structure

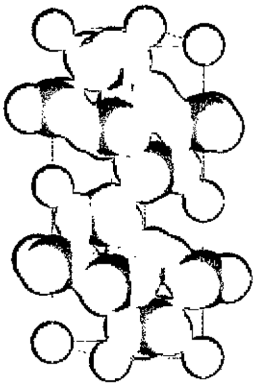

Figure E.1: The unit cell of calcite[26]

Figure E.2: Photograph of aragonite[27]

Figure E.3: Aragonite crystals (~ 4 cm in size)[28]

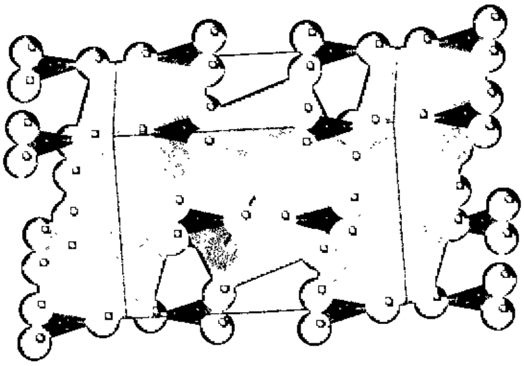

Figure E.4: Crystal structure of aragonite. O is red, Ca blue and C black. Carbonate groups are black triangles[29]

Figure E.5: White needle shaped aragonite crystals, Aragon, Spain[30]

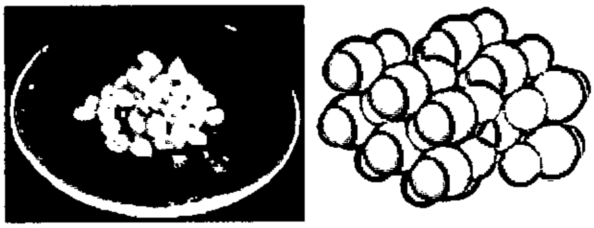

Figure E.6: Crystal of sodium hydroxide[25]

Figure E.7: Calcium hydroxide powder[24]

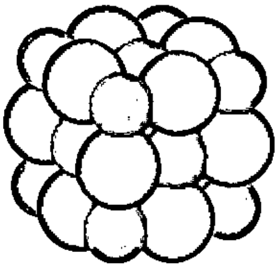

Figure E.8: Calcium oxide marble size[23]

Appendix -F

Electrolytic Cells Process

Appendix- F Electrolytic Cells Process

(i) Mercury Cells Process

The mercury cell actually involves two cells. In the primary electrolyzer (or brine cell), purified saturated brine containing approximately 25.5 wt% sodium chloride flows through an elongated trough that is inclined slightly from the horizontal. In the bottom of this trough a shallow sheet of mercury, the cathode, flows concurrently with the brine. Closely spaced above the cathode, an anode assembly is suspended which consists of horizontal block of graphite or dimensionally stable (titanium-base) anodes. Current flowing through the cell decomposes the brine that passes through the narrow space between the electrodes, liberating chlorine gas at the anode and sodium metal at the cathode. The chlorine gas is accumulated above the anode assembly and discharged to the purification process. Figure F.1 shows mercury cells process flow sheet.

[1]As it is liberated at the surface of the mercury cathode, the sodium immediately forms an amalgam which essentially eliminates the reaction with water in the brine to form caustic soda and hydrogen, and reaction with dissolved chlorine[3].

Decomposer

Form the electrolyzer, dilute amalgam is fed to a separate packed-bed reactor (the decomposer, denuder, or soda cell) where it reacts with water

$$Na\text{-}Hg + H_2O \longrightarrow Na^+ + OH^- + \tfrac{1}{2} H_2 + Hg$$

Mercury cells are usually operated so as to maintain a 21-22 wt% concentration of salt in the spent brine discharging from electrolyzer. This corresponds to a decomposition of 15-16% of the salt during a single pass[3].

Mercury Losses

The mercury used in a mercury cell represents a significant portion (10-15%) of the total investment in the cell. Depending on the cell size, the amount required ranges from 680-1360 kg / (t.d) (1360 to 2720 lb per short ton per day) of chlorine capacity. Prior to government regulation, mercury losses from mercury cell plants ranged from 135-225 g/t chlorine. At the operating temperatures of electrolyzers and decomposers, mercury has a measurable vapor pressure; even with cooling, mercury is lost in the product and waste streams from a plant. Recent EPA regulations limit effluent discharge to 0.28 g mercury per metric ton of product chlorine for existing plants with additional 50% reduction for new plants. To meet these regulations, in addition to elaborate filter systems, mercury cell plant have also had to install more efficient coolers to condense mercury vapor[3].

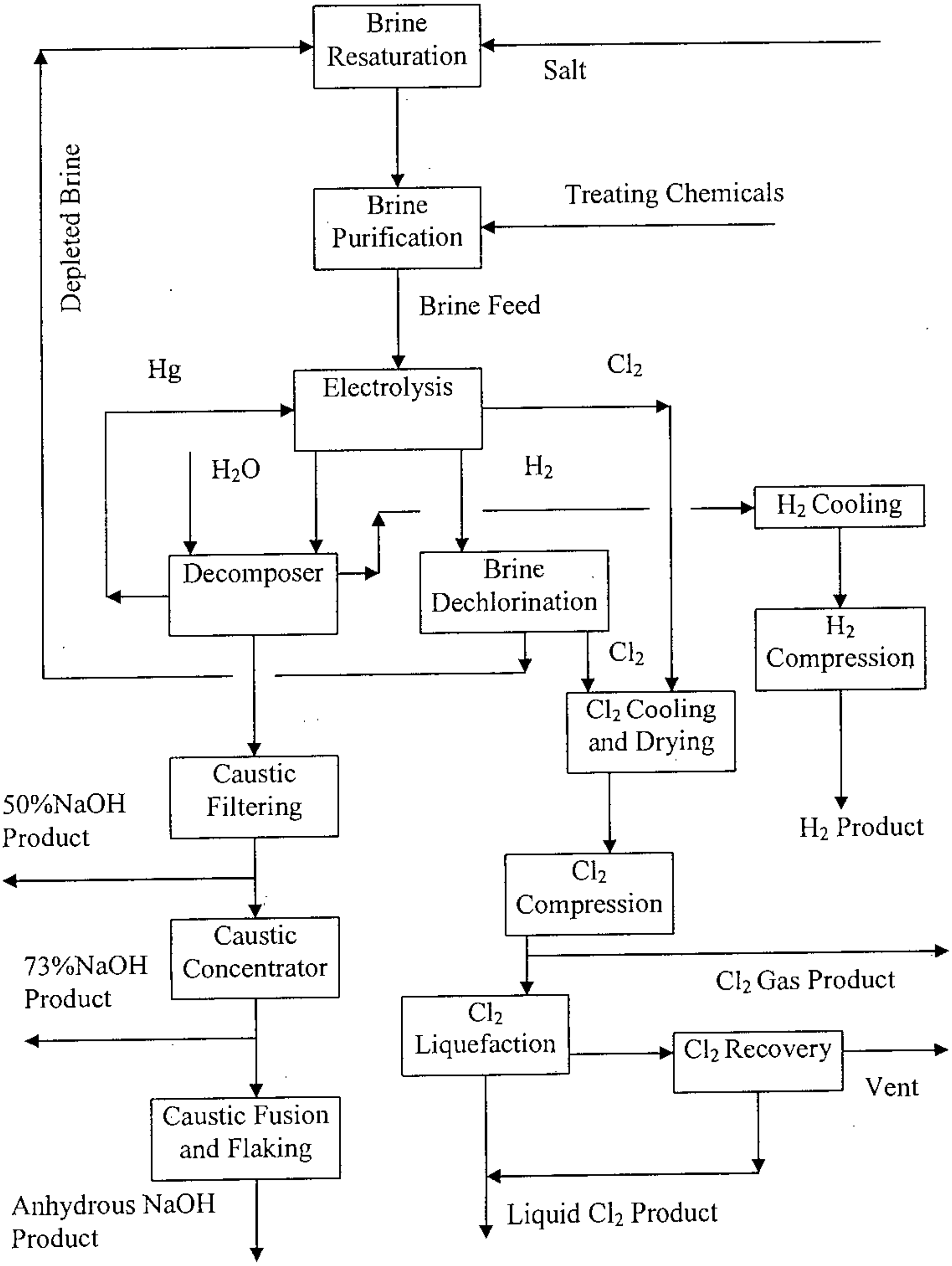

Figure F.1: Mercury cells process flow sheet[3]

(ii) Diaphragm Cells Process

Chlor-alkali diaphragm cells produce chlorine and sodium hydroxide by electrolysis of saturated brine. A diaphragm is employed to separate the chlorine liberated at the anode, and the caustic soda produced at the cathode. Without the diaphragm to isolate them, the caustic soda and chlorine would react to form sodium hypochlorite, with further reaction to produce sodium chlorate. Modern diaphragm cells employ vertical electrodes and a cathode-supported diaphragm. Asbestos is vacuum-deposited on the cathode to form the diaphragm, which separates the feed brine, or anolyte, from the caustic-containing catholyte. Purified brine enters the anode compartment and percolates through the diaphragm into the cathode chamber[3].

In diaphragm cell, saturated brine (25 wt% NaCl solution) is decomposed to approximately half of its original concentration in a pass through the electrolyzer as compared to a 16% decomposition of salt per pass in mercury cells. Electrolytic decomposition of water and hypochlorous acid forms oxygen at the anode. When dimensionally stable anodes are used, oxygen leaves the cell with the chlorine. With graphite anodes, some of the oxygen reacts with graphite and / or the binder to form carbon dioxide. Graphite particles breaks off, tending to plug the diaphragm, with a resulting gradual loss of diaphragm permeability. After 90-100 days of operation the diaphragm becomes inoperable and the asbestos must be replaced. Precipitation of calcium and magnesium hydroxide on the catholyte side of diaphragm may also create blocking problems. Hydrochloric acid is added to the brine entering the anode compartment to neutralize back migrating hydroxyl ions and to suppress formation of hypochlorous acid, both of which are damaging to graphite[3].

As in mercury cells, chlorine discharges from the anode compartment, together with small amounts oxygen, carbon dioxide, and hydrogen. The catholyte solution discharging from cell contains about 10-12% caustic soda and 14% sodium chloride. Figure F.2 shows diaphragm cells process flow sheet[3].

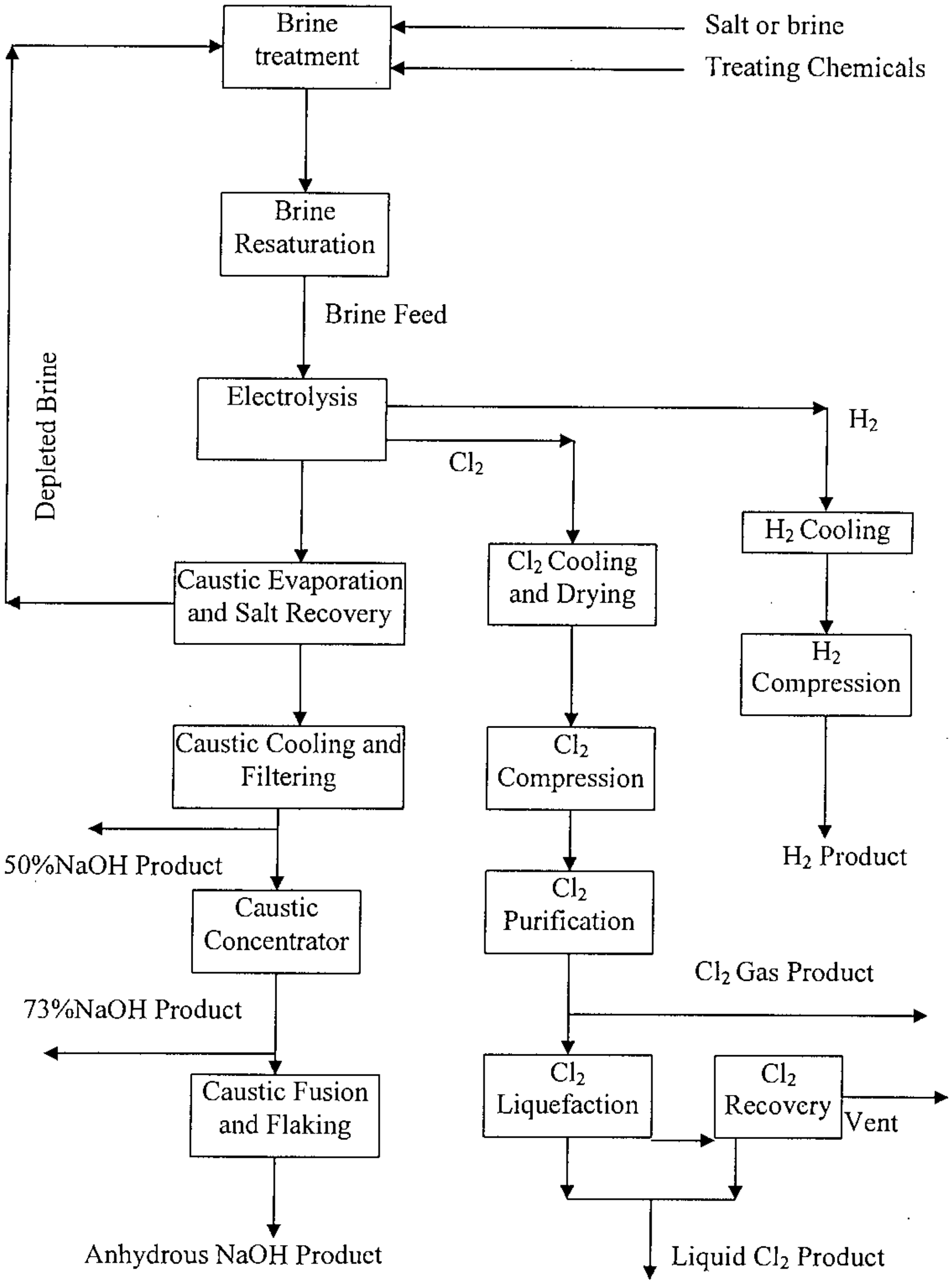

Figure F.2: Diaphragm cells process flow sheet[3]

(iii) Membrane Cells Process

In the membrane process, the anode and cathode are separated by an ion-exchange membrane that selectively transmits sodium ions, but suppresses the saturation migration of hydroxyl ions from the cathode into the anode.

1. A brine solution is fed into the anode compartment, where chlorine gas is produced, and sodium ions migrate into the cathode through the membrane.
2. Depleted brine is discharged from the cell.
3. In the cathode compartment, hydrogen is produced at the cathode, leaving hydroxyl ions which, together with the sodium ions that have crossed the membrane, form caustic soda.
4. Pure water is added to the catholyte to control the concentration of the caustic soda solution.

Chloride ions in the anolyte are excluded by the ion exchange membrane, so the rate of diffusion of chloride ions from the anolyte to the catholyte is extremely low. As a result, a high purity caustic solution is produced as the catholyte effluent. Since the catholyte is strongly caustic, there is some back migration of hydroxyl ions from the catholyte into the anolyte. Figure F.3 shows the membrane cells process flow sheet.

The membrane is the key component of the membrane cell. Its primary requirements are durability during electrolysis, high selectivity for sodium ion transport, low electrical resistance, and sufficient mechanical strength for practical use. The energy requirements and the quality of the solution depend on the membrane. Only ion exchange membranes made of perfluoro polymer can withstand severe conditions of exposure to chlorine and caustic soda at high temperatures. This process produces a higher percentage caustic soda solution (33-35 wt%), with very low sodium chloride content.

Advantages of the membrane process include its energy efficiency, which allows for less costly cell operations, and its ability to produce with no asbestos or mercury environmental contaminants. Disadvantages include the high purity brine solution requirement and the high cost of the membrane itself.

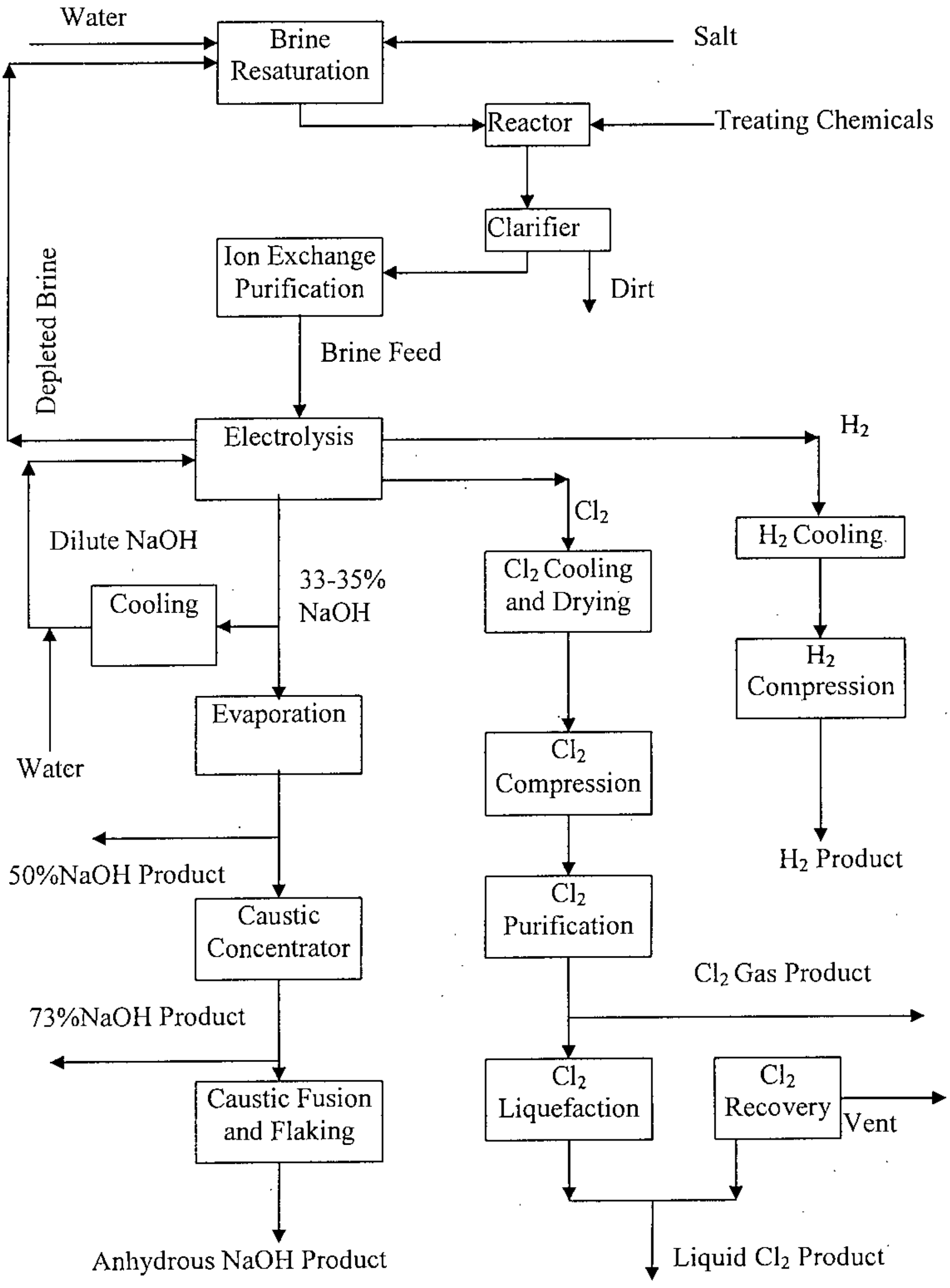

Figure F.3: Membrane cells process flow sheet[21]

Appendix –G

Correction on Previous Work

Appendix-G **Correction of Previous Work on Causticization**

Sample Calculation Used by Imtiaz[8]

Reactants:

Na_2CO_3: 100 g

$Ca(OH)_2$: 76.8 g (10% excess)

Water: 785 ml

Sample Calculation

Multistage Recovery of Caustic Solution after Causticizing with Analytical Grade lime. (Ref. Table 5.2.1)

Table A.4: Results for titration of caustic solutions

	Total Volume of Solution, ml	Volume of caustic stock solution titrated, ml	Volume of HCl at phenolphthalein end point, ml	Volume of HCl at methyl orange end point, ml	Strength of HCl, N
Decantation and vacuum filtration	415	10	60.7	63.3	0.486
1st recovery stage	165	10	28.9	29.7	0.486
2nd recovery stage	150	10	13.1	13.5	0.486
3rd recovery stage	105	10	7.4	7.6	0.486

Decantation and vacuum filtration stage

For 10 ml of stock solution

Volume of HCl required to neutralize OH^- and convert

CO_3^{2-} to HCO_3^- $v = 60.7$ml

Volume of HCl required to neutralize OH^- and CO_3^{2-}, $V = 63.3$ ml.

Therefore, volume of HCl required to neutralize OH^- $= v - (V - v)$
$= 60.7 - (63.3 - 60.7)$

$= 58.1$ ml

Volume of acid required to neutralize $CO_3^{2-} = 2(V - v)$

$= 2 \times 2.6$

$= 5.2$ ml

Wt. of NaOH in 10 ml stock solution = 1.13 g

Total wt. of NaOH in 415 ml solution = 46.87 g

Wt. of Na_2CO_3 in 10 ml stock solution = 0.139

Total wt. of Na_2CO_3 in 415 ml solution = 5.55 g

Using the above procedure;

For 1st recovery stage

Total wt of NaOH recovered = 9.01 g

Total wt of Na_2CO_3 recovered = 0.68 g

For the 2nd recovery stage

Total wt. of NaOH recovered = 3.703 g

Total wt. of Na_2CO_3 recovered = 0.31 g

For the 3rd recovery stage

Total wt. of NaOH recovered = 1.47 g

Total wt. of Na_2CO_3 recovered = 0.108 g

Total wt. of recovered NaOH = (46.87 + 9.01 + 3.70 + 1.47) g

= 61.06 g.

% Recovery $= \frac{61.06}{71.7} \times 100\%$ ← *Inconsistent, because 100 g Na_2CO_3 was used to perform causticization and theoretical production should be 75.47 g*

$= 85.16\%$

Correction

Theoretical production of NaOH = 75.47 g (instead of 71.7 g used by Imtiaz[8])

Actual obtained NaOH = 61.06 g and Na_2CO_3 = 6.65 g

Actual equivalent Na_2CO_3 recovered = 61.06 × 1.325 + 6.65 = 87.55 g

% recovery of equivalent Na_2CO_3 = 87.55%

Apparent conversion of Na_2CO_3 = 61.06/75.47 = 80.91%

Counting loss, actual conversion of Na_2CO_3 = 80.91/0.8755 = 92.4%

Calculation Procedure Used by Mannan[9]

Detailed Calculations

Experiment carried out at 100 °C (AR Grade Reagents).

Raw materials:	Na_2CO_3 = 125g,	dissolved in	Water = 500ml
	$Ca(OH)_2$ = 90.9g	dissolved in	Water = 364ml

Volume of stock solution = 750ml, made to 1000ml with distilled water

Volume of wash solution = 500ml.

Mass of dry filter cake = 126.3g.

Strength of standard $HCl_{(aq)}$ = 0.2504N

Table B1. Results for Titration of Stock Solution

Vol. of Stock Solution	Vol. of $HCl_{(aq)}$ (Methyl Orange)	Vol. of $HCl_{(aq)}$ (Phenolphthalein)
10ml	78.9ml	72.4

Table B2. Results for Titration of Wash Solution

Vol. of Stock Solution	Vol. of $HCl_{(aq)}$ (Methyl Orange)	Vol. of $HCl_{(aq)}$ (Phenolphthalein)
10ml	23.9ml	22.2

For 10ml of stock solution

Volume of acid required to neutralize OH^- and CO_3^{2-} = 78.9 ml

Volume of acid required to neutralize OH^- = 72.4 ml *(incorrect procedure)*

Therefore, Volume of acid required to neutralize CO_3^{2-} = 6.5 ml *(incorrect procedure)*

Na_2CO_3 unreacted in 10 ml of stock solution = 6.5 * 0.2504 = 1.628 meqv.

Na_2CO_3 unreacted in 1000ml stock solution = 162.76 meqv.

For 10ml of wash solution

Volume of acid required to neutralize OH^- and CO_3^{2-} = 23.9 ml *iIncorrect)*

Volume of acid required to neutralize OH^- = 22.2 ml *(incorrect)*

Therefore, Volume of acid required to neutralize CO_3^{2-} = 1.8 ml

Na_2CO_3 unreacted in 10 ml of wash solution = 1.8*0.2504 = 0.451 meqv.

Na_2CO_3 unreacted in 500ml wash solution = 22.54 meqv.

Total Na_2CO_3 unreacted = 162.76 + 22.54 = 185.3 meqv

Total Na_2CO_3 taken = 125g = 2358 meqv

Total Na_2CO_3 reacted = 2172.7 meqv

% Conversion of Na_2CO_3 $= \frac{2172.7}{2358} * 100$ = 92.1% *(incorrect)*

Concentration of NaOH in original stock solution

$$= \frac{72.4*0.2504}{10} * \frac{1000}{750} = 2.417\ N$$

$$\cong 2.417 * 40\ g/lt = 96.7\ g/lt$$

$$\cong 9.7\ wt.\ \%$$

Correction

For Stock Solution

Volume of HCl required to titrate OH^- only = 72.4-(78.9-72.4) = 65.9 ml

Strength of NaOH= 65.9 × 0.2504/10 = 1.65 N

Mass of NaOH = 1.65× 40 = 66 g

Strength of Na_2CO_3 = 6.5× 2×0.2504/10 = 0.3255 N

Mass of Na_2CO_3 = 0.3255 × 53 = 17.25 g

For Wash Solution

Volume of HCl required to titrate OH^- only = 22.2-(23.9-22.2) = 19.5 ml

Strength of NaOH= 19.5 × 0.2504/10 = 0.4883 N

Mass of NaOH = 0.4883 × 40/2 = 9.77 g

Strength of Na_2CO_3 = 1.7× 2×0.2504/10 = 0.0852 N

Mass of Na_2CO_3 = 0.0852 × 53 = 2.26 g

Total NaOH produced = 66+9.77 = 75.77 g

Na_2CO_3 unreacted = 17.25 + 2.26 = 19.51 g

% Recovery based on equivalent Na_2CO_3 = [19.51+75.77 × 1.325]/125 = 95.9%

% conversion = 84.4% (basis: unreacted Na_2CO_3)

Correction for Other Calculated Data to Generate Graph

Ratio of present and previous (Mannan[9]) calculated value = 84.4/92.1 = 0.916

Table G.1: Calculated Data of Mannan[9] after correction

Temperature, ^0C	Analytical Grade Reactants	Commercial Grade Reactants
60	82.94	69.30
80	85.30	72.40
90	85.60	75.10
100	84.40	72.95